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WATER POLLUTION BY THALLIUM AND RELATED METALS

CALSPAN CORPORATION

PREPARED FOR
ENVIRONMENTAL PROTECTION AGENCY

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T. R. Magorian, K. G. Wood, J. G. Michalovic, S. L. Pek, M. W. Van Lier

Calspan Project No. ND-5189-M-1

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ABSTRACT

During this project, Calspan personnel sampled smelter and mill wastewater outfalls, receiving water, slag heaps, tailings ponds, and streams, and coal-burning facility fly ash dumps. The amount of heavy metals in sediment is greater at any given time than that dissolved in water, and hence floodwater erosion of particulate matter presents a hazard. Up to 17% lead, 0.1% cadmium and 5 ppm thallium were found in sediments of streams used for irrigation and drinking water below copper and zinc extractive industries in high runoff regions.

Groundwater infiltration in the Northwest and Ozarks provides mine drainage water which is used in mills and/or concentrators. This volume of water transports toxic wastes into naturally erosive bottom sediments thereby contaminating the food chain.

Some techniques to prevent hazardous spills and effluent treatment methods were evaluated and recommendations made.

Heavy metal concentrations in water and biota are higher in the fall at low water following benthic accumulations during the growing season. Metal pickup by algae was measured in the laboratory.

Procedures for detecting and measuring the amount of thallium by atomic absorption in the presence of high concentrations of chloride and other ions were developed. The overall sensitivity achieved for thallium is approximately 0.1 ppb in water. The detection limit for thallium in biota is typically 10 ppb and in sediment, 80 to 90 ppb because of interferences present in any given sample.

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SECTION I

CONCLUSIONS

Based on samples and data collected in 1972 and 1973, the following conclusions are drawn.

High levels of toxic metals were found in the particulate matter discharged from northwestern mills, smelters and refineries, especially from old smelters such as East Helena, Montana. Levels were lower in the New Missouri lead belt and very low at White Pine, Michigan on Lake Superior. Fine granulated slag and tailings have a large surface area for leaching and are subject to catastrophic erosion.

Hazardous concentrations of over 15 ppm thallium, 17% Pb and 0.1% Cd have been found in stream sediments below metal sulfide processing facilities (Table 1).

Data from the study show a definite tendency for heavy metals to accumulate in rooted plants in greater concentrations than in algae, fish or other biota.

The estuarine plants, refineries, and those riparian plants on large rivers were the most serious polluters since they dispose of wastes directly into the water body through outfalls. Smelters and mills (concentrators) have extensive cinder banks and tailings ponds along the rivers. The greatest potential threat is transport of particulate matter by floodwater.

In general, the volume of toxic metal in the moving sediment of the streams is much greater than the amount in the water at any given time. There is little observable bioconcentration through food chains as compared to sediment concentration of the more toxic metals, especially thallium.

Since the thallium is tied up in the sediments and very little of the sediments from the smelters or natural thalliferous occurrences reaches the oceans, the low concentration of thallium in the oceans as compared with the concentration in freshwater runoff is believed to be associated with the reduction of thallic to thallous ion with substitutions of the latter for potassium in clays.

Indium was rarely found above background but was concentrated enough to report for Tacoma (Table 13) and Kellogg (Table 19).

TABLE 1.

THALLIUM CONCENTRATIONS

BIOTA	PARTS/MILLION
Kellogg, Bunker Hill copper smelter, horsetail roots under stack	2.8
Kellogg, S. Fork Coeur d' Alene R., cranefly in water	2.8
East Helena, Prickly Pear Ck., cattail roots in smelter pond	1.0
Tacoma, ASARCO, horsetail leaves under stack	0.77
Kellogg, S. Fork Coeur d' Alene R., grass roots in water	0.59
Kellogg, Bunker Hill copper smelter, horsetail leaves under stack	0.5
East Helena, ASARCO, zinc smelter runoff, _Spirogyra_	0.49
Anaconda, Warm Springs Creek, stonefly larvae below old mines	0.45
Tacoma, Pt. Defiance, _Ulva_ on beach at smelter	0.28
Tacoma, ASARCO, horsetail roots as above	0.22
East Helena, Prickly Pear Ck., cattail leaves	0.063
Kellogg, S. Fork Coeur d' Alene R., _Spirogyra_	0.061
East Helena, Prickly Pear Ck., slime on _Spirogyra_ diatomaceous	0.012

TABLE 1 (CONT'D)

THALLIUM CONCENTRATIONS

WATER	PARTS/MILLION
Kellogg:	
Slag runoff after leaching	0.11
Mill outfall	0.02
Granulating water	0.015

SEDIMENT	PARTS/MILLION
Kellogg, mud	15
Butte, Silver Bow Creek, crust below Anaconda Mill	10
Tacoma, ASARCO copper slag bottom with live prawns	9.1
East Helena, ASARCO zinc smelter, septic ooze	8.6
Kellogg, S. Fork Coeur d' Alene R., mud below slag and outfalls	4.9
Kellogg, Bunker Hill zinc plant, Govt. Gulch	1.7
Kellogg, Bunker Hill copper smelter, soil under stack	1.1
Butte, Silver Bow Ck., bottom soil below Anaconda mill	0.61
Butte, Silver Bow Ck., mud below Anaconda mill	0.52
Basin, mud from ruined mill	0.44
Kellogg, Govt. Gulch mud below Bunker Hill zinc plant	0.42
Selby, ASARCO lead smelter, soil under stack	0.32

SECTION II

RECOMMENDATIONS

The following recommendations are offered:

Care and perhaps EPA inspection should be expended in the proper construction of retaining dams.

Recycling of water should be used wherever possible, not just where water is scarce or expensive.

Treatment of any water discharged with basic hydroxides and sulfide can be used to recover metals. (Although the effluent may be more alkaline than ideal, it will be less toxic. Alkalinity can be reduced by recarbonation.)

Close surveillance of sulfide processes should be implemented by mine owners in humid regions where floods and excess water process occur, particularly where dams are only constructed of tailings.

Separation of mine drainage waters from mill wastes should be accomplished to reduce the volume of muddy water in contact with tailings.

Slag granulation should be avoided since it encourages heavy metal leaching thereby contaminating large volumes of cooling water.

Further field studies and analyses are needed to define the the industrial toxic metal threat more precisely, particularly on more generally-polluted rivers such as the Ohio, Illinois and Raritan.

SECTION III

INTRODUCTION

Toxic metals are widely distributed in their natural state. Traces of these compounds are found in a wide variety of rocks and fuels, and commonly occur in association with ores of commercial importance, such as the ores of copper, lead, and zinc. One such group of toxic metal compounds involves the element, thallium.

Actual production and use of thallium in the United States is small; currently about 7,000 pounds per year. Since the demand for Tl is limited by its toxicity and price, American Smelting & Refining Company (Asarco) supplies the domestic market from its Denver, Colorado cadmium smelter. Other Tl concentrates are dumped on cinder banks and into tailing ponds where they present a potential pollution hazard.

Commercially, the small amount of thallium produced is recovered from the cadmium-bearing flue dusts of zinc smelting operations. Most of these flue dusts are returned to the smelter but may be stored in waste cinder banks, which are thus a source of pollution due to the leaching action of rainwater upon the soluble thallium salts present, or to erosion of the waste banks. Thallium pollution may also result from the sudden discharge of residues and spillage of waste liquors from a variety of refining and chemical operations, including lead and copper refining, sulfuric acid and pigment manufacture, and almost all fuel-burning processes. Additional damage to the aquatic environment may also occur from accidental spills during the manufacture, transport, storage and use of commercially-produced thallium and its compounds. The toxic compounds of other metals such as cadmium, lead, arsenic, indium, and selenium, which are related to, or associated with, thallium-bearing ores, are concentrated in similar waste deposits and can also damage the aquatic environment.

Tl tends to concentrate in the tailings, waste liquors and dusts of smelters, refineries, pigment plants using sphalerite blende (ZnS), galena (PbS) and calcopyrite ($CuFe\,S_2$) which are processed in the greatest quantities.

A chart showing the flow of thallium-bearing minerals from mines to disposal areas and suspected entry to aquatic environments is shown in Figure 1.

A comprehensive program was conducted to determine the occurrence and movement of thallium and related toxic metals from ore refining and chemical operations to water bodies. This involved sampling and chemical analysis of water sediments and biota from all possible sources

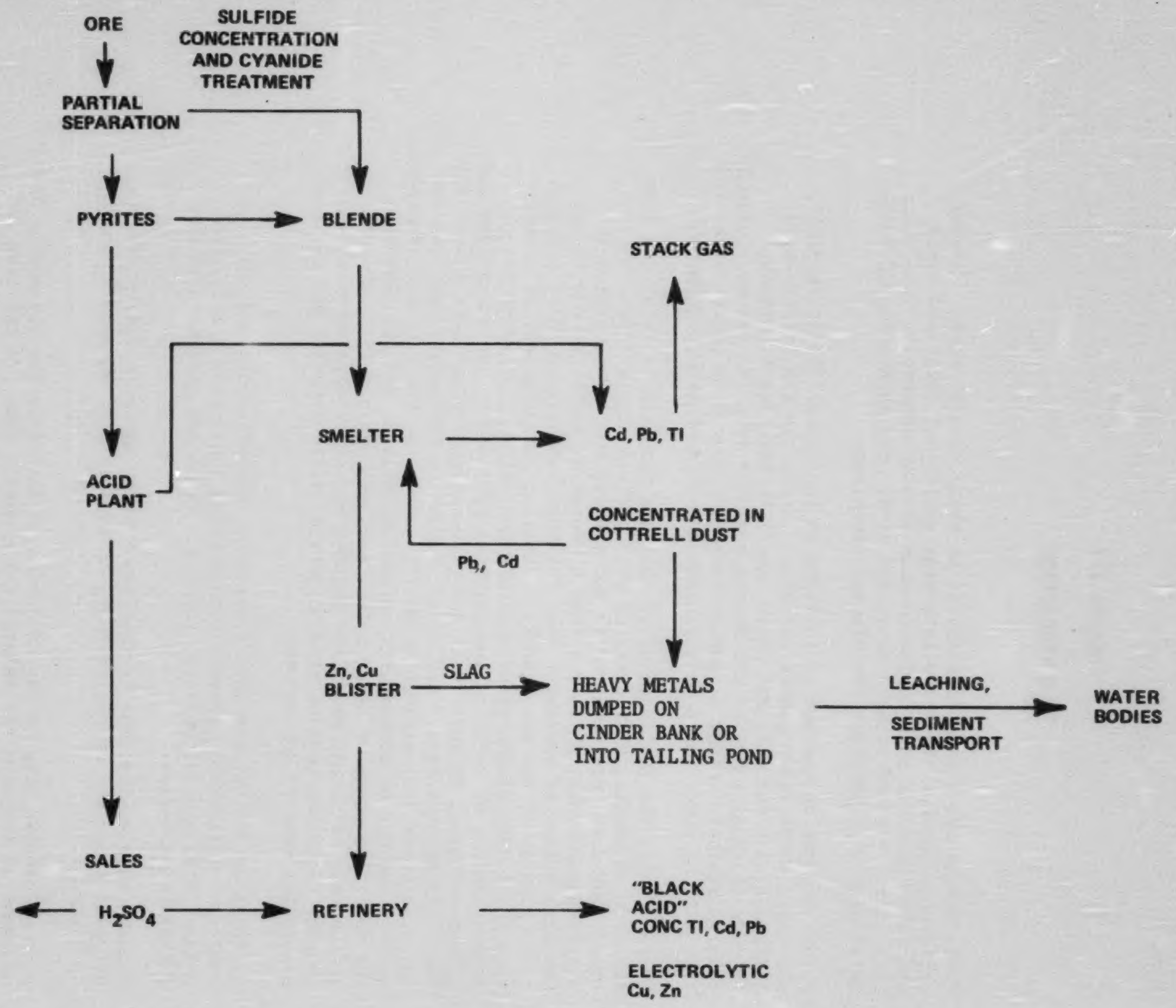

FIGURE 1 FLOW CHART OF INDUSTRIAL THALLIUM CONCENTRATION

and sinks at a site. Sources included slag piles, cinder banks, land fills, and effluent discharges.

Primary sinks include the water and sediments of receiving water bodies and ground water. Water biota serve as secondary sinks for thallium and related metals by uptake, first as dissolved or complexed ions and later by passage through food webs. The hydrology of the disposal areas was of critical interest. Field examinations indicated the potential pattern of runoff and erosion.

A The sampling program was planned and carried out so as to elucidate the extent of movement and concentration of thallium and related metals in physical and biological compartments of the aquatic environment. The potential magnification of heavy metal concentration through the food chain has been carefully investigated at contaminated sites, clean control sites, and in the laboratory.

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SECTION IV

METHODS, CONTROLS AND PROCEDURES

Water, sediment and biota were sampled at each site, taking into account that leaching and other run-offs may be dependent upon the action of rain or flood water.

Samples were collected from all drainage ditches, outfalls, and storm sewers emanating from or passing through areas where thallium from ore refining might be present. Additional samples were collected from the receiving bodies of water. Still further control sampling was conducted on upstream portions of the receiving bodies of water so that background levels of thallium and other metal concentrations were established. These background levels are needed to confirm whether or not thallium and other toxic metal concentrations in water bodies, suspected of contamination from the ore refining operation, are significantly greater than normal background level.

Glass bottles were used for sampling from outfalls, ditches and storm sewers, and shallow receiving streams. Deep bottom water was collected using a Kemmerer bottle. Because the solubility of most metal compounds is low, it was expected that water concentrations would often be in the part per billion range. Therefore, up to two gallons were collected for each sample so as to comprise sufficient quantity for repeated chemical analyses.

Controls

It was necessary to establish control stations in regions of the country which have different bedrock geochemistries because background levels of metals in soils and drainage waters will differ depending on the local geochemistry. A meaningful comparison of sites from different regions of the country can be made only when background levels are subtracted. Where plants are located in close proximity within a region of similar geochemistry, it was possible to use one control station for more than one plant.

Regional backgrounds were highest in the Pacific Northwest due to active volcanism. Uncontaminated algae from Waldport, Oregon, for example, contained 48 ppm zinc, 29 ppm copper, 48 ppm lead, 900 ppb indium, 10 ppb thallium and less than 2 ppm cadmium. Mayflies from the nearby Nestucca

River contain 62 ppm zinc, 52 ppm copper, 17 ppm lead, 1 ppm indium but less than 10 ppb thallium and 3 ppm cadmium.

Analytic controls (blanks) were carried in the field and quadruplicate water samples collected, some of which were spiked with known quantities of metal nitrates in the field. Blanks showed less than 100 ppb zinc, 200 ppb copper, 20 ppb cadmium, 10 ppb lead, 100 ppb indium, and .1 ppb thallium. Equipment used for biological sampling included dip nets, plankton nets, drift nets, and Kemmerer bottles for bulk water dwelling organisms. Guidance on sampling, sorting, and preservation of biological samples was provided by the EPA.

Because of the low solubility of most heavy metal compounds, these metals are more likely to be associated with sediments than with water. In addition, the electrical ionic charges present in fine sediments (i.e., clay, fine silt) attracts free ions of thallium and other metals. Thus, metals are associated with fine sediments. Under turbulent and high water flow conditions, considerable quantities of sediments are carried as suspended sediments. Suspended sediments were separated from water in the field and analyzed separately. Collected bed load sediments were elutriated to separate silt and clay sized particles from sand. These fractions were analyzed separately wherever possible.

Collection and chemical analysis of receiving-water biota were conducted to determine the extent to which thallium and associated heavy metals are accumulated in biota as a result of effluents attributable to ore refining and chemical operations. Particular attention was given to sampling at various trophic levels in food webs to ascertain whether or not bioconcentration of metals occurs through food chains.

Specific aquatic food chain species were sampled and analyzed according to the type of water body, geographical location, and degree of pollution. Figure 2 is a model of the food chains sampled in streams. The lines connect various trophic levels from which representative species or groups of species were sampled. At the bottom of the food chain, stream detritus and algal plankton were sampled. Proceeding up the food chain, we sampled benthic organisms such as nymphs, larvae, snails and bivalves which feed principally from plankton as well as oligochaete worms and chironomids. Still higher in the food chain, predatory nymphs were sampled. Finally, at the top of the aquatic food web, fish were sampled.

The food chain shown in Figure 2 is general in nature for a mature unpolluted river. The food web for estuaries where some metal refineries are located was different. Some of the receiving streams, such as the South Fork of the Coeur d'Alene at Kellogg, Idaho, are polluted and contain only pollutant tolerant organisms such as sludge worms, midge larvae, and sewage maggots and larvae.

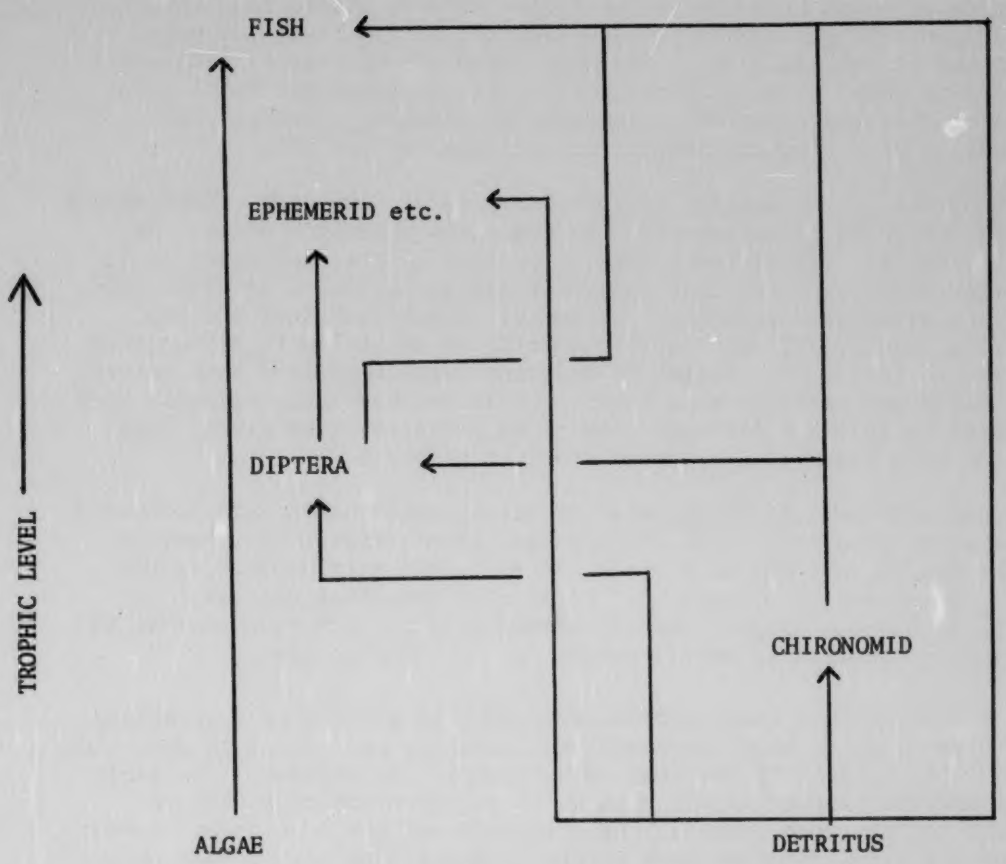

FIGURE 2. SIMPLIFIED FOOD-WEB FOR THE BIOTIC COMMUNITY IN A RIVER.

FROM: AQUATIC PRODUCTIVITY
W.D. RUSSELL-HUNTER
MACMILLAN, 1970

Sample Preparation

Routine procedures for preparing water, biological and sediment samples prior to analyses were as follows:

Water Samples

Water samples were acidified by the addition of 1 ml of concentrated nitric acid to a 200 ml sample in its original collection vessel. Sample volume was at least 200 ml. The sample was shaken vigorously and analyzed after settling of particulate matter.

Sediment Samples

The bulk of the sediment samples were analyzed for available metals. Extraction was by a 24-hour exposure of 2 grams of the sample to 2 ml of a 1:1 mixture of concentrated nitric and hydrochloric acid at 50°C. Since the moisture content of the samples as collected varied widely, two-gram portions were dried and weighed prior to extraction. Metal content is reported on a dry weight basis. The acid solution was diluted to 20 ml with distilled water prior to analysis.

Biological Samples

Biological sample analysis was on a wet weight basis with excess (surface) moisture removed at the sampling location. Digestion was performed in the collection containers to avoid loss of material and contamination of samples. Sample weight was obtained by subtracting the predetermined bottle weight from the weight of container plus sample. A 3.5:1.5 mixture of concentrated nitric and perchloric acids was then added to the sample on the basis of 1 ml per gm of sample. Digestion was accomplished with the bottle sealed at 50°C for 24 hours. The acid solution was then diluted 5:1 with distilled water for analysis.

A number of sample preparation procedures are available ranging from 24-hour room temperature digestion with trichloracetic acid to high temperature digestion with perchloric and nitric acids.(2) Experience at this laboratory during conduct of the research has shown that metals tightly bound in organics are often not recovered by room-temperature digestion procedures, but are satisfactorily recovered at 50°C. Digestion by perchloric and nitric acids with heat was therefore used.

Extraction with acid was suitable alone only for concentrated samples. More dilute samples required concentration, particularly by MIBK chelation described in Table 2. A number of chemical procedures were employed to the different samples for analysis, and to improve detection capabilities where detection of extremely low levels was sought. These included acid extractions, digestion procedures, and the concentration of metals by means of substituted dithiocarbamate chelates.

Some of the other preparation methods used in the program are shown in Tables 3 and 4. The sulfide precipitation method described in Table 3 was required for samples of extremely low metal concentrations.

TABLE 2.

COMPLEXATION METHOD FOR THALLIUM

A. The following reagents are prepared:

1. Diethydithiocarbamate (DDC) -- Twenty grams of diethydithiocarbamic acid sodium salt are mixed with 380 ml of distilled water. This solution is filtered through a 0.45 micron filter. The filtrate is extracted twice with 15 ml portions of MIBK.

2. MIBK -- 4-methyl -2- pentanone (Eastman).

3. Phthalate buffer -- 102 g of Baker Reagent grade potassium biphthalate are dissolved in distilled water and diluted to 500 ml. Fourteen ml of 1M HCl are added and the resulting solution diluted to 1.0 liter.

4. Sodium hydroxide and hydrochloric acid to adjust pH.

B. All glassware must be rinsed with 1:1 HNO_3 containing a small amount of HF followed by rinsing with distilled water, acetone and more distilled water.

C. Procedure

1. A sample aliquot is diluted to 100 ml with distilled water.

2. Add 2 ml of buffer and adjust pH to 3.6 ± 0.1.
Add 7.0 ml of DDC solution.
Shake vigorously for 30 seconds.
Withdraw MIBK layer.
Evaporate MIBK to dryness.
Add 2.5 ml of concentration HNO_3 + 2.5 ml of distilled water.
Sample is ready for analysis.

TABLE 3.

SULFIDE PRECIPITATION PROCEDURE

1. Exactly 10.0 ml of sample was acidified with 1 ml of HNO_3 and 1 ml of HCl.

2. The pH was then adjusted to 12 with 2.5 M sodium hydroxide.

3. 0.5 g of Na_2S dissolved in 1 ml of water was added.

4. When no observable precipitate formed, 1 ml of 1000 ppm Zn and 1 ml of 1000 ppm Pb were added.

5. The resulting solution was filtered through a millipore HWAG 0.45 micron filter.

6. The precipitate was redissolved in 5 ml of concentrated nitric acid and made up to 10 ml in a volumetric flask with distilled water.

7. Sample was then ready for subsequent analysis.

TABLE 4.
SAMPLE DIGESTION WITH VARIOUS ACIDS

Volatilization of some metal compounds during digestion with perchloric, sulfuric and phosphoric acids at 200-220°C. (in % of the element volatilized)

Procedure 1. ($HClO_4$ - HCl): 20 to 100 mg of the chloride are treated with 15 ml of 60% $HClO_4$; the temperature is raised to 200°C; 15 ml of HCl are slowly added (during 15 minutes) while the temperature is kept at 200-220°C.
Procedure 2. ($HClO_4$ - H_3PO_4 - HCl): as Procedure 1 except that 15 ml of $HClO_4$, 5 ml of 85% H_3PO_4 and HCl are used.
Procedure 3. (H_2SO_4 - HCl): as Procedure 1, $HClO_4$ being replaced by H_2SO_4 (d = 1.84).
The following elements are not volatilized by any of these procedures: Ag, alkali metals (Na, K, Rb, Cs), Al, Ba, Be, Ca, Cd, Co, Cu, Fe, Ga, Hf, In, Ir, Mg, Ni, Pb, Pd, Pt, rare earths, Rh, Si, Ta, Th, Tl, U, W, Zn, and Zr.

Elements	Procedure 1 $HClO_4$ - HCl	Procedure 2 $HClO_4$ - H_3PO_4 - HCl	Procedure 3 HCl - H_2SO_4
As (III)	30	30	100
As (V)	5	5	5
Au	1	0.5	0.5
B	20	10	50
Bi	0.1	0	0
Cr (III)	99.7	99.8	0
Ge	50	10	90
Hg (I)	75	75	75
Hg (II)	75	75	75
Mn	0.1	0.02	0.02
Mo	3	0	5
Os	100	100	0
P	1	1	1
Re	100	80	90
Ru	99.5	100	0
Sb (III)	2	2	33
Sb (V)	2	0	2
Se (IV)	4	2.5	30
Se (VI)	4	5	20
Sn (II)	99.8	0	1
Sn (IV)	100	0	30
Te (IV)	0.5	0.1	0.1
Te (VI)	0.1	0.1	0.1
Tl	1	1	1
V	0.5	0	0

SOURCE: PINTA, 1971

Atomic Absorption Analysis

All samples were analyzed for thallium, indium, lead, cadmium, zinc and copper by atomic absorption spectrophotometry. Selected samples were also analyzed for tellurium.

A Perkin-Elmer Model 303 modified by Calspan personnel to increase its sensitivity was used. Improved electronics provided detection limits substantially lower than the normal instrument for some elements, and direct digital readout in concentration was also used. The instrument was equipped with a deuterium-arc background corrector, and both a sampling boat accessory and a heated graphite atomizer were available. The single beam option provided improved absorption peak definition and greater determination accuracy when it could be used. An emission correction circuit was added to sense the emission from the flame and automatically subtract this signal from the photomultiplier output. The amount of emission was indicated linearly on a meter mounted on top of the electronics box with readings of 25 (center scale) for zero emission and 40 for an emission level of 25% of the hollow cathode light intensity.

The detection limit for thallium by boat in the atomic absorption (AA) flame was 1 part per billion (ppb). By using a volumetric syringe, the precision could be held within 10% at 20 ppb or 5% at 50 ppb. Other detection limits for aqueous solutions using the Perkin-Elmer Model 303 are shown in Table 5.

Electrochemical Analysis

A second evaluation method used was the application of anodic stripping voltammetry. This technique has been employed for ppb-level determination of many heavy metals, including Ag, Cd, In, Pb, Tl and Zn. The thallous ion gives a strong polarographic wave at -0.475V in 1M solutions of potassium nitrate, chloride, sulfate and hydroxide.

Two Anodic Stripping Voltammetry water samples from the Kellogg site were run for Tl with anodic stripping voltammetry (ASV) at the courtesy of Dr. Eric Zink of Environmental Science Associates, Burlington, Massachusetts, who makes the equipment. Lead and cadmium were measured simultaneously on 50 microliter aliquots of each sample added to 5 milliliters of 1N sodium acetate adjusted to pH 5.3. Copper and thallium were measured using 5 milliliter aliquots of each sample. These aliquots were evaporated to dryness and taken up in 5 milliliters of 1N sodium acetate and 0.1 ml 6M HCl. Copper was measured by plating at -0.5 voluts, and then thallium was measured by plating at -1.0 volts after addition of 0.2 milliliters of an 0.1N EDTA solution. Some results are shown in Table 6. With the exception of copper in the second sample, agreement with AA is reasonably close indicating that the AA determinations are fundamentally reliable.

TABLE 5. CALSPAN ATOMIC ABSORPTION DETECTION LIMITS IN AQUEOUS SOLUTIONS AND COMPARISON WITH ELECTROCHEMICAL ANALYSES*

Element	Detection Limit (ppm) Flame	 Heated Graphite Atomizer
Thallium	0.02	0.001
Cadmium	0.004	0.00002
Lead	0.03	0.0004
Indium	0.05	0.01
Copper	0.005	0.0005
Zinc	0.005	0.0005

Sample	Metal	Concentrations - ppm AA	 ASV
Slag Runoff	Tl	0.1	0.1
	Cd	1.0	0.75
	Cu	0.03	0.029
	Pb	Not Available	1.8
Smelter Weir	Tl	0.02	0.036
	Cd	2.2	1.6
	Cu	0.03	0.086
	Pb	5.3	4.1

* Samples from Kellogg Site.

SECTION V

EVALUATION OF DATA FROM SITES

Site Selection

Sites were selected from those refining and chemical operations which produce residues and waste liquors containing toxic metal compounds. They included zinc smelters, lead refineries, copper refineries, steel mills, sulfuric acid plants, lithopone plants and fuel burning plants in close proximity to watercourses.

Selected sites were sampled in sufficient detail to provide a picture of the course of thallium pollution into and through the aquatic environment. Representative smelters, fuel-burning powerplants and steel mills were selected which discharge into relatively clean fluvial and estuarine waters. Those streams with more downstream human ultimate consumption were emphasized.

The overall site selection with reasons for and against their selection are listed in Table 6.

The locations of selected sites are shown on an index map (Figure 3).

The list does not include scrap smelters because their starting material contains much less Tl, and it is believed that significant concentrations of Tl should be quite rare at such smelters. The plants listed in Table 6 are near water bodies used by large populations. All of the significant sites drain directly into water bodies.

Copper and lead-zinc sulfide ore milling, smelting and refining produce the bulk of the thallium pollution problem. Although it was not possible to test all such facilities operating in this country with the funds available, the sites selected were believed typical or worse relative to operating procedures for waste disposal and were situated on streams of ecologic significance.

In the processing sequence from sulfide ore to metal product, mining creates coarse dumps which can leach slowly and be eroded by streams. Milling produces large quantities of fine tailings which can be leached rapidly. Containment is now attempted for most active mills, although removal by flood erosion still occurs rarely at some large ponds such as at Anaconda. Smelting, by hot reduction and oxidation, releases metals as air pollution and produces slag, which is leached and washed away.

TABLE 6.

SITE SELECTION GUIDE

SITES	SAMPLING ORDER	ARGUMENTS FOR	ARGUMENTS AGAINST
CORNING	1	PRELIMINARY	
HAYDEN	6	BEING STUDIED BY G. RATHBUN	
VIBURNUM	5	CLEAN WATER, BEING STUDIED BY J. WIXSON	PROBABLE LOW Tl
WHITE PINE	2	LAKE SUPERIOR	
KELLOGG	3	TOXIC DUST	
ANACONDA	3		
TACOMA	3	SALMON	DIFFICULT SAMPLING PROBLEM
EL PASO	6	IRRIGATION	
PALMERTON	4	CADMIUM REFINING	
ANTHRACITE	1	FUEL BURNING	POSSIBLE LOW Tl STANDBY, CLOSED OR RUINED
SELBY	2	ON SAN FRANCISCO BAY	CLOSED
EAST HELENA	3	TOXIC DUST	SMALL STREAMS
BUTTE	3	LOW pH	
BASIN	3	OPEN FLUE, DUMP IN RIVER	RUINED
BETHLEHEM	4	ANTHRACITE COKE	NO LONGER USED
EAST ST. LOUIS	5	IN MISSISSIPPI RIVER FLOOD PLAIN	
GLOVER	5	INTO BIG RIVER	RECIRCULATION
HERCULANEUM	5	ON MISSISSIPPI RIVER	
ST. FRANCOIS	5	OLD LEAD MILL	STANDBY

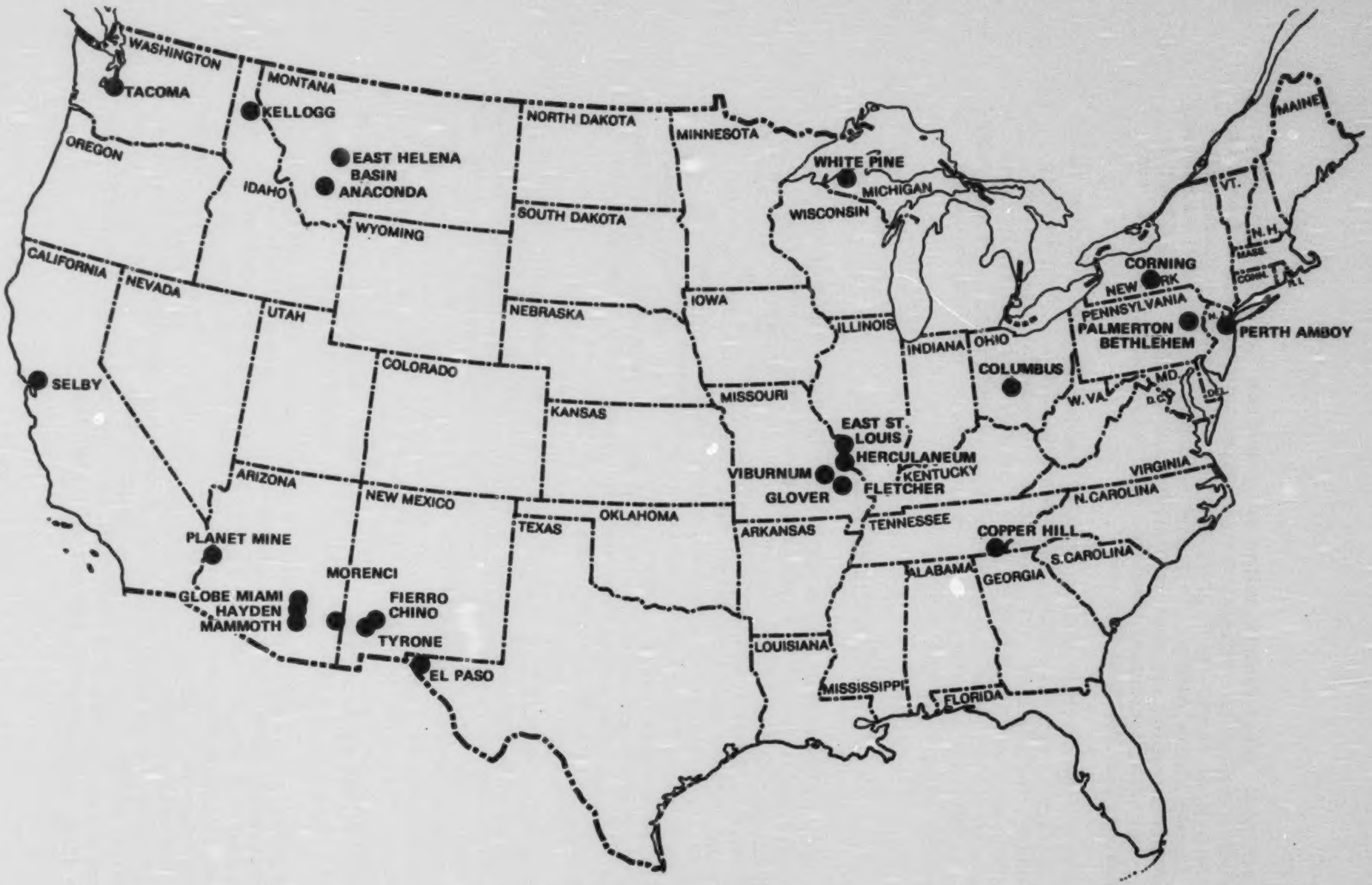

Figure 3 SITE LOCATIONS

The effluent metal concentrations are relatively low. The tank house or final electrolytic refining step is often integrated in the smelter complex, as at Tacoma and Kellogg sites, to utilize acid produced from the smelter sulfur oxides. This acid is released, often without recovery of unsalable byproducts such as thallium and arsenic. The effluent is often reused at integrated plants so that metals are recycled or concentrated at a few final outfalls.

The processing at these older plants is similar to that described in the section on the White Pine, Michigan site although the operating conditions and ore characteristics vary. In general, the western smelters are larger and further from byproduct markets. Their ores, formed at higher temperatures, are richer in additional sulfides, selenides, tellurides and arsenides, such as those of thallium which are released during milling and smelting.

Tacoma, Washington

The ASARCO copper smelter and refinery is on Puget Sound at the mouth of Commencement Bay and the adjacent Dalco Passage between Point Defiance and Vashon Island (Figures 4&5). The estuary was sampled in September 1972 and resampled in May 1973. Tables 7-13 contain the data on thallium and other metals from various locations shown in Figure 4. It is important to note where "none" is indicated in Tables 7-13 and all following tables on heavy metal analyses of collected samples that the type of material (i.e., slag, mud, biota) was not present and therefore not sampled. In many cases, we believe that fish and bottom organisms were not present as a consequence of the high toxic metal concentration or low pH.

Concentrate imported from the Phillippines is predominantly enargite (Cu_3AsS_4) with significant gold, silver and pyrite. In addition, arsenical materials from ASARCO operations at Battle Mountain, Nevada and El Paso, Texas are processed. The blister copper produced at Tacoma has the highest present concentrations of silver and arsenic, and its lead concentration is exceeded only by the Carteret scrap smelter among U.S. plants. The copper is refined by electrolysis in hot acid. The acid at Tacoma is heated to 145°F in Pb tubes and purified in lead-lined cells before discharge into the Sound. The slag is granulated in a stream of water in order to allow it to deposit in deep water.

The plant waste banks, effluent and waters as far out as possible were sampled from a boat. Dredgings near the principal outfall yielded only shell fragments of dead marine bivalves (scallops and razor clams) in iron-rich mud to a water depth of 200 feet (approximately 1/2 mile offshore). Green algae was collected from rocks on shore adjacent to the acid outfall, and also at a location at the north end of the smelter area growing on one of the older slag deposits which form the entire smelter site. Barnacles (Balanus) were also collected at these same sites. In the tidal littoral zone, barnacles (as plankton filter feeders) live closer to the outfalls than algae.

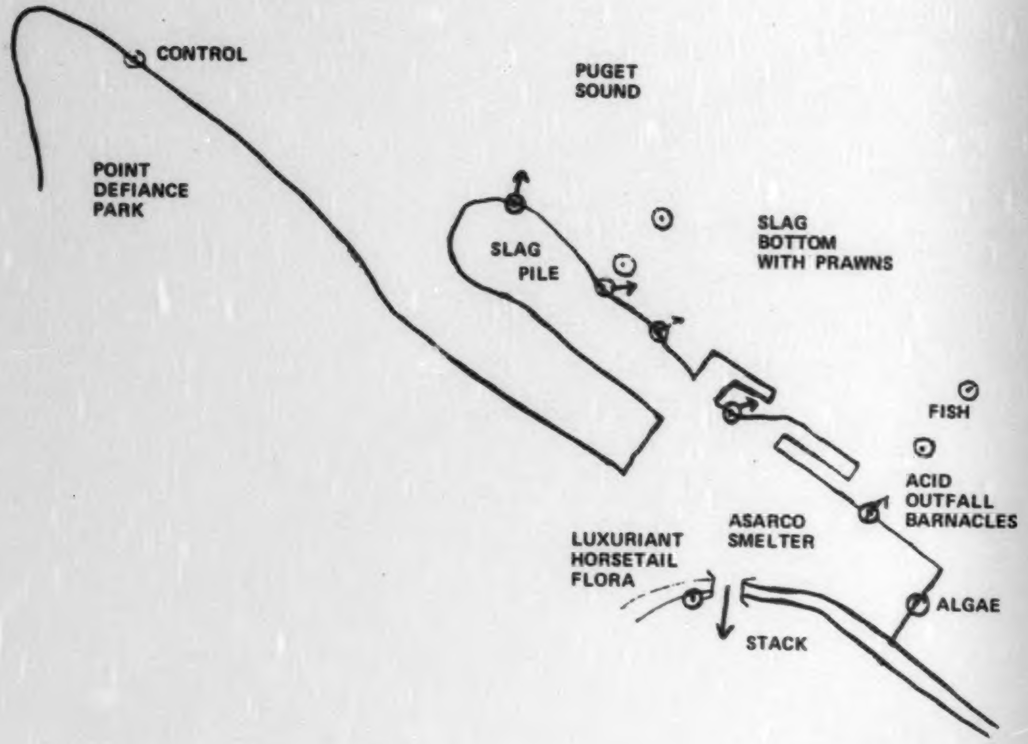

Figure 4 SKETCH OF TACOMA SMELTER

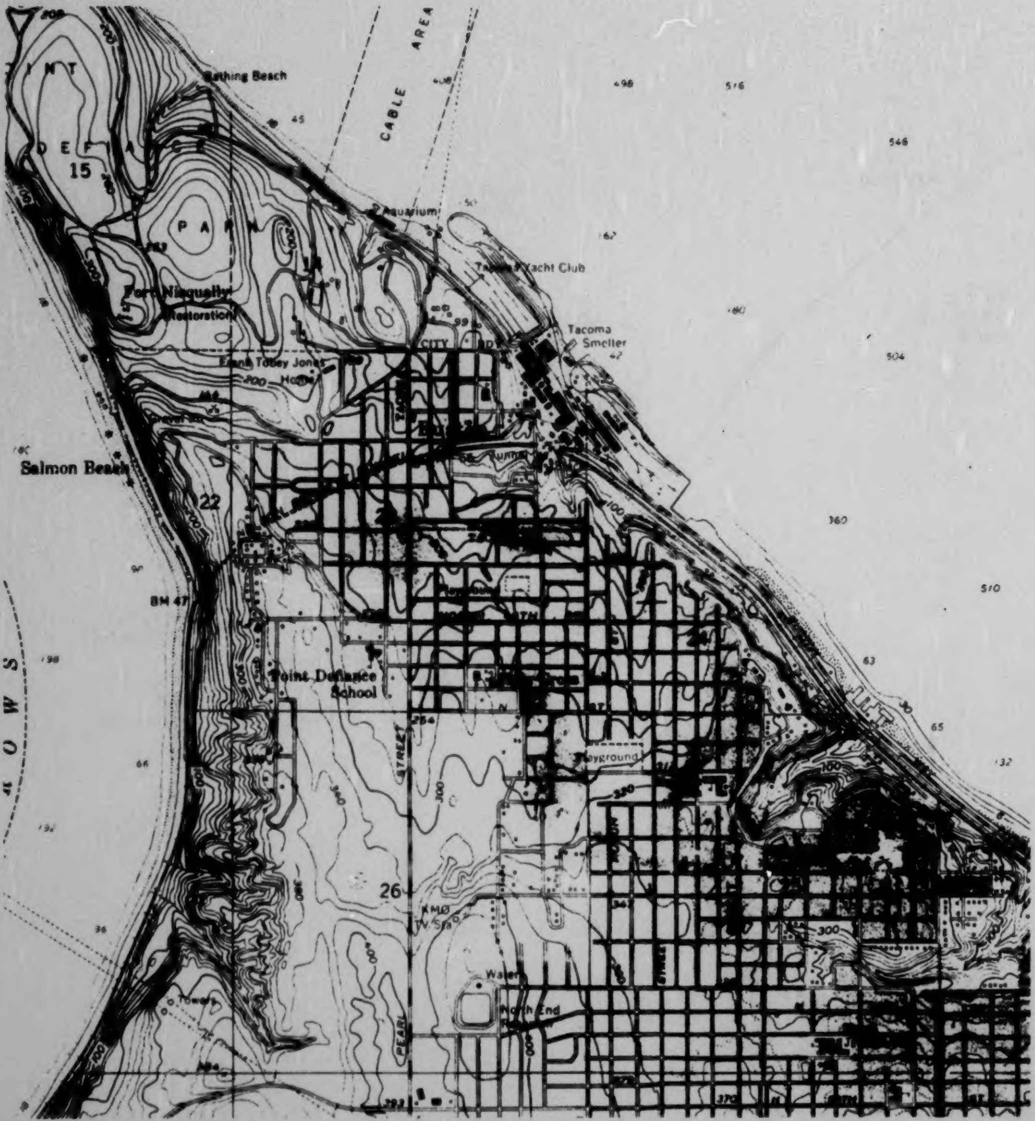

Figure 5 TOPOGRAPHIC MAP OF THE TACOMA, WASH. AREA

TABLE 7.

TACOMA -- THALLIUM CONCENTRATION -- ppm September 1972

SAMPLING LOCATION	WATER	CLAM SHELLS*	GREEN (Ulva)	HORSETAILS UNDER STOCK
CONTROL	<0.01	<.46	< .28	
POTENTIAL SOURCES:				
SMELTER	2.4		.28	leaves .77
SLAG	<.01-2	9.1		roots .22

* DEAD, ABRADED CARBONATE FRAGMENTS FOUND IN TOXIC MUD NEAR ACID OUTFALL-- (PRELIMINARY DETERMINATION, NOT REPRODUCED) AND CONTROL AT POINT DEFIANCE.

TABLE 8.

ASARCO - TACOMA May 1973
THALLIUM concentration - ppm

	pH	water	mud	algae	invertebrates	fish
control	5.	<.0001	<.1	<.008	<.01	---
acid outfall	3.8	.0012	0.52	<.007	<.06	perch (1972) <.06
dock outfall	4.2	.00015	none	<.02	<.06	flounder <.03
slag	5.	.002	0.31	none	9.1	none

TABLE 9.

ASARCO - TACOMA May 1973

CADMIUM concentration - ppm

	Water	Mud	Algae	Invertebrates	Fish
control	0.003	0.11	<2	---	---
acid outfall	0.04	2.8	<1.8	<2.9 shells 5.5	0.44
dock outfall	0.015	none	2.8	<6.4	<4
slag	0.004	3.5	none	none	none

Table 10.

ASARCO - TACOMA May 1973

LEAD concentration - ppm

	Water	Mud	Algae	Invertebrates	Fish
control	0.02	0.26	<11	---	---
acid outfall	0.4	2400	440	140	12
dock outfall	0.015	none	84	<44	66 spleen 310
slag	0.02	1700	none	none	none

Table 11.

ASARCO - TACOMA May 1973

COPPER concentration - ppm

	Water	Mud	Algae	Invertebrates	Fish
control	0.03	96	<5	---	---
acid outfall	0.04	2500	440	220	19
dock outfall	0.24	none	360	58	10
slag	0.2	3400	none	none	none

Table 12.

ASARCO - TACOMA May 1973

ZINC concentration - ppm

	Water	Mud	Algae	Invertebrates	Fish
control	0.27	130	3.3	---	---
acid outfall	7.2	6200	160	190	18
dock outfall	1.1	none	110	22	40
slag	0.26	8000	none	none	none

Table 13.

ASARCO - TACOMA May 1973

INDIUM concentration - ppm

		Water	Mud	Algae	Invertebrates	Fish
	control	0.3	---	0.4	---	---
29	acid outfall	0.4	45	3	15 shells 21	---
32	dock outfall	0.1	none	2	<.6	10
	slag	0.5	35	none	none	none

Gill nets were set adjacent to the acid outfall to the southeast of the smelter. A number of crustacean larvae (Metanaupliae) were pulled off the net from shallow water. In addition to the three marine fish previously taken by gill net, a large flounder was caught off the dock. Liver, kidney and muscle samples were taken. Between sampling periods, the acid outfall had been plugged and effluent was then diverted through a lime pit, raising the pH slightly, and allowed to seep into the ground. Although an elaborate liquid SO_2 plant financed by the state is under construction, no further work was yet underway on the apparent arsenic or heavy-metal problems which are evident in the data presented in Tables 8-13 for the samples collected in May 1973.

Shells of dead clams pave the muddy bottom in front of the acid discharge. They average 5.5 ppm Cd, 50 ppm Pb, 100 ppm Cu and 220 ppm Zn; Tl is undetectable.

Only Equisetum, seemingly the most tolerant terrestrial vegetation, grows in the dust beneath the stack. The brown algae, Fucus and Laminaria were taken along the beach at Pt. Defiance, as were additional green algae NW of the smelter. This location, upwind in a strong tide rip, is believed to be relatively free of smelter pollution.

Selby, California

A few reconnaissance samples were taken on 27 August 1973 from the abandoned ASARCO non-ferrous smelter at Selby, California.[*] This site, which has been used for nearly a century has a large pile of slag poured into the bay. Sediment, algae, water and a representative small fish were collected on the beach eroded into the slag pile. In addition, bay water from across the Carquinez Straits and Pacific Ocean water from off Monterey were sampled for comparison

Lead at a concentration of 3 ppm along with 240 ppb copper and 450 ppb zinc were found in a stagnant pond draining the slag pile.

The pond and its outfall (diluted by the bay tide) show no excess cadmium over controls (50-100 ppb) from elsewhere in the bay. Green algae (Ulva) near the outfall contain 5.2 ppm lead (as compared with 3.6 ppm across the straits at Neare Island) and 0.18% zinc (as compared with 4.7 ppm). Cadmium and copper were not significantly concentrated, nor were the other samples. Thallium was not detected except in soil near the stack at 320 ppb.

Kellogg, Idaho

The Bunker Hill and associated smelters fill Government Gulch and the adjacent South Fork of the Coeur D'Alene River. The situation is

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[*] It is historically interesting that Cottrell's first precipitator was operated in the acid plant at this facility (Figure 6).

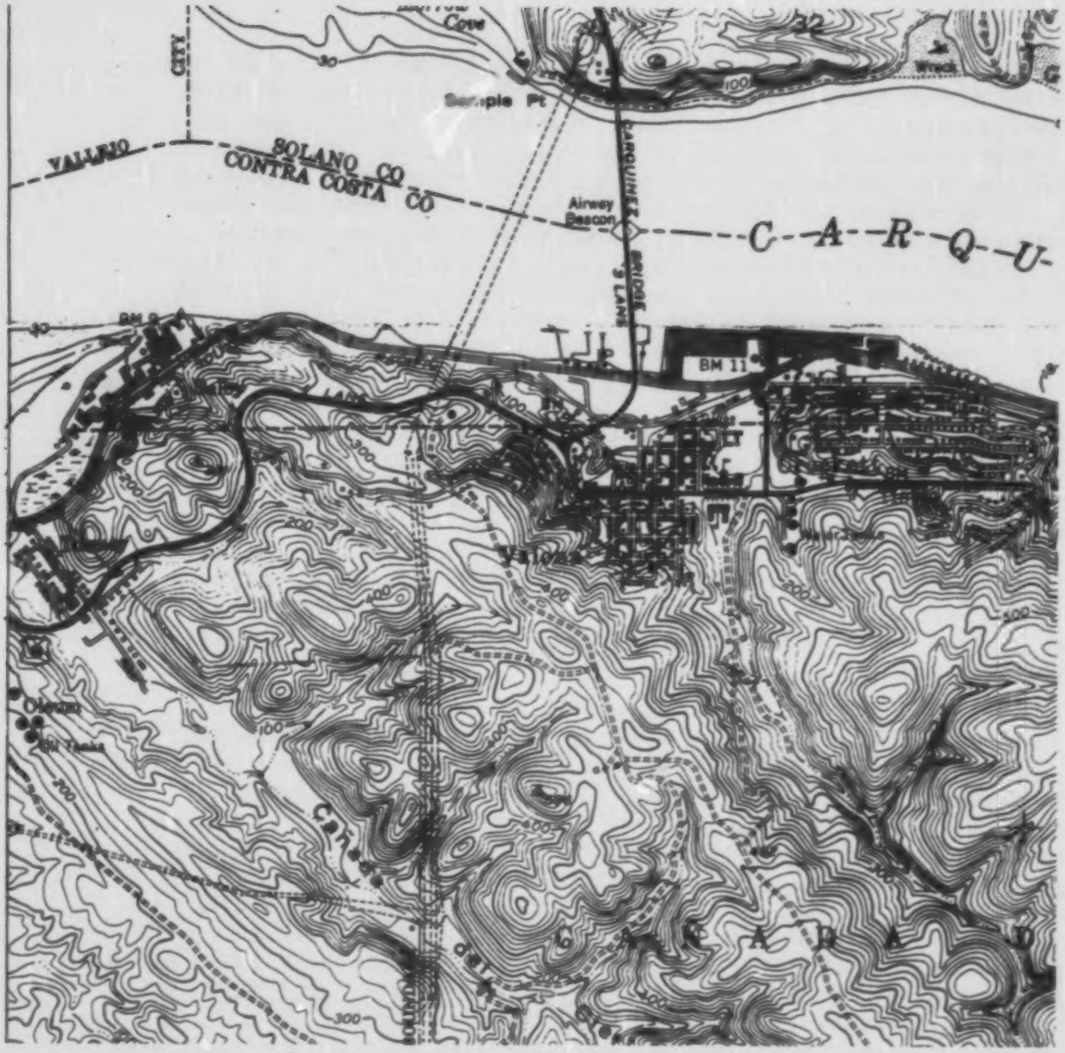

Figure 6 TOPOGRAPHIC MAP OF SELBY, CALIFORNIA AREA

potentially one of the most hazardous in the country. The entire complex drains acidic effluent into heavily inhabited but barren gulches. The smelter stack emissions in Government Gulch have killed nearby vegetation.

Bunker Hill has hundreds of acres of tailings ponds for over four miles in the flood plain of the South Fork of the Coeur d' Alene River, from Kellogg to Pine Creek. The high rainfall of the area provides continual leaching of these huge expanses of tailings. Although now protected by low levees, much of the toxic material has been flooded and leached by excessive runoff from the large cutover drainage basin. Large quantities of various sulfide-processing waste water are discharged into the river at all flows. It has received mining and raw domestic wastes for over 80 years. In addition to present tailings (contained since 1968), floods release significant quantities of zinc and other heavy metals from the old stream sediments. The zinc and phosphate plants dump acidic effluent into a heavily inhabited area. Human exposure to cadmium and lead is relatively high (Hammer et al., 1972). Thallium was found in Government Gulch in particulates and mud below the Bunker Hill zinc plant; however, pipe was being laid to divert these wastes into the main tailings pond on the valley flat.

This complex was sampled as far downstream as the level of Coeur D'Alene Lake. Figure 7 shows the locations sampled and Figure 8 is a topographic map of the area. The results of this sampling are contained in Tables 14 through 19.

This district has yielded ores worth well over a billion dollars in lead, zinc, copper and silver since 1879. The mines occur within an area about 25 miles long and 15 miles wide. The country rocks consist of Pre-Cambrian Pritchard black shale, 2-1/2 miles thick, which has been intruded by monzonite very similar to the Boulder granodiorite of Montana. The most productive mines (Sunshine and Bunker Hill) are found along great faults continuing east into Montana; the Osborn fault has a vertical displacement of 3 miles or more and a horizontal displacement measured in tens of miles. Between these great faults are minor faults and shear zones that have been filled and replaced to form the lodes. They attain 7,000 feet in length, average 9 feet in width and have been followed downward over 5,300 feet.

The ores consist of disseminated galena, zinc blende, pyrite and argentiferous tetrahedrite. Some pyrrhotite, boulangerite, magnetite, arsenopyrite and some copper minerals occur in minor amounts. The ores carry approximately 6 per cent lead, 3 per cent zinc and 2 ounces of silver per ton.

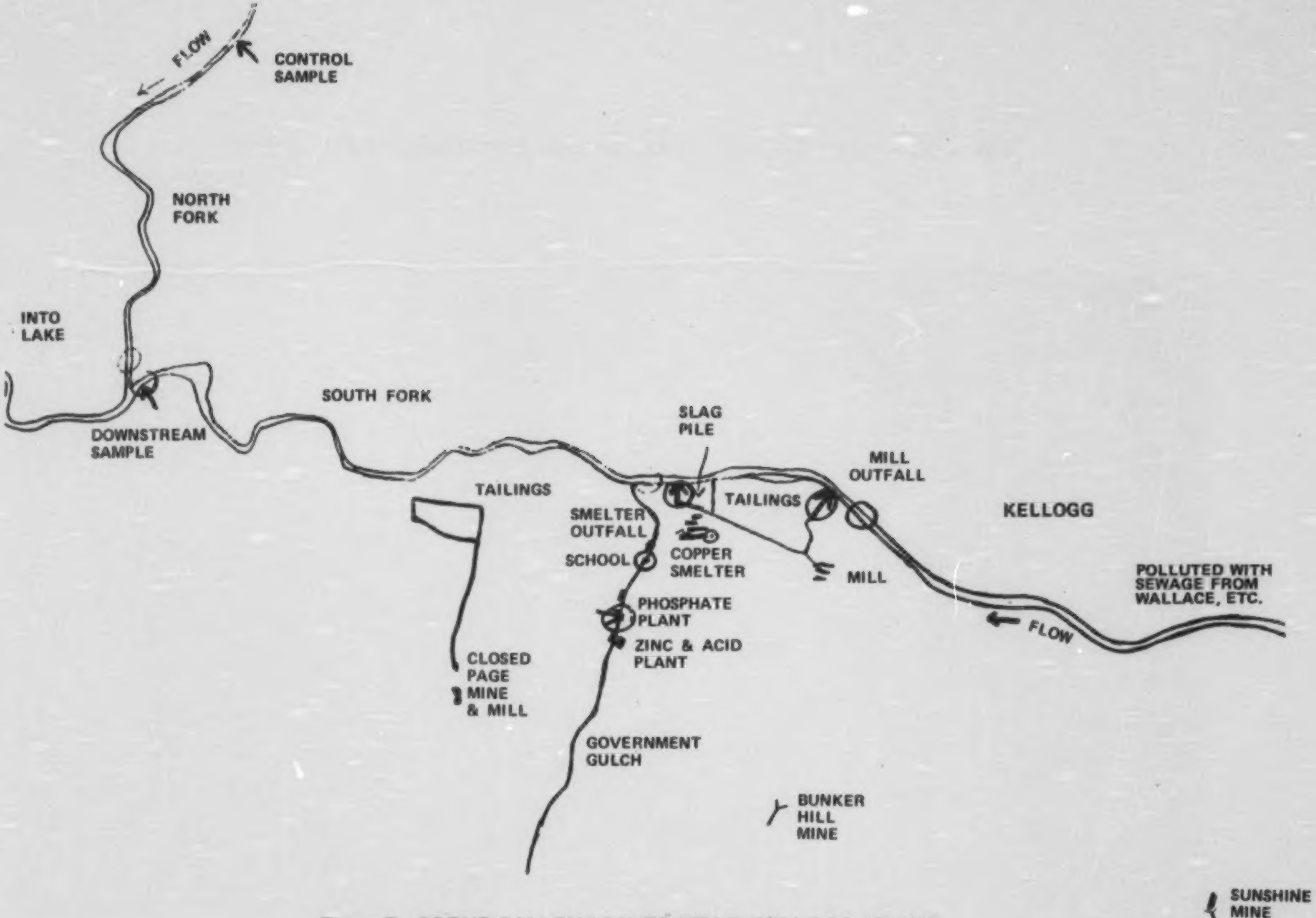

Figure 7 COEUR D'ALENE RIVER NEAR KELLOGG, IDAHO

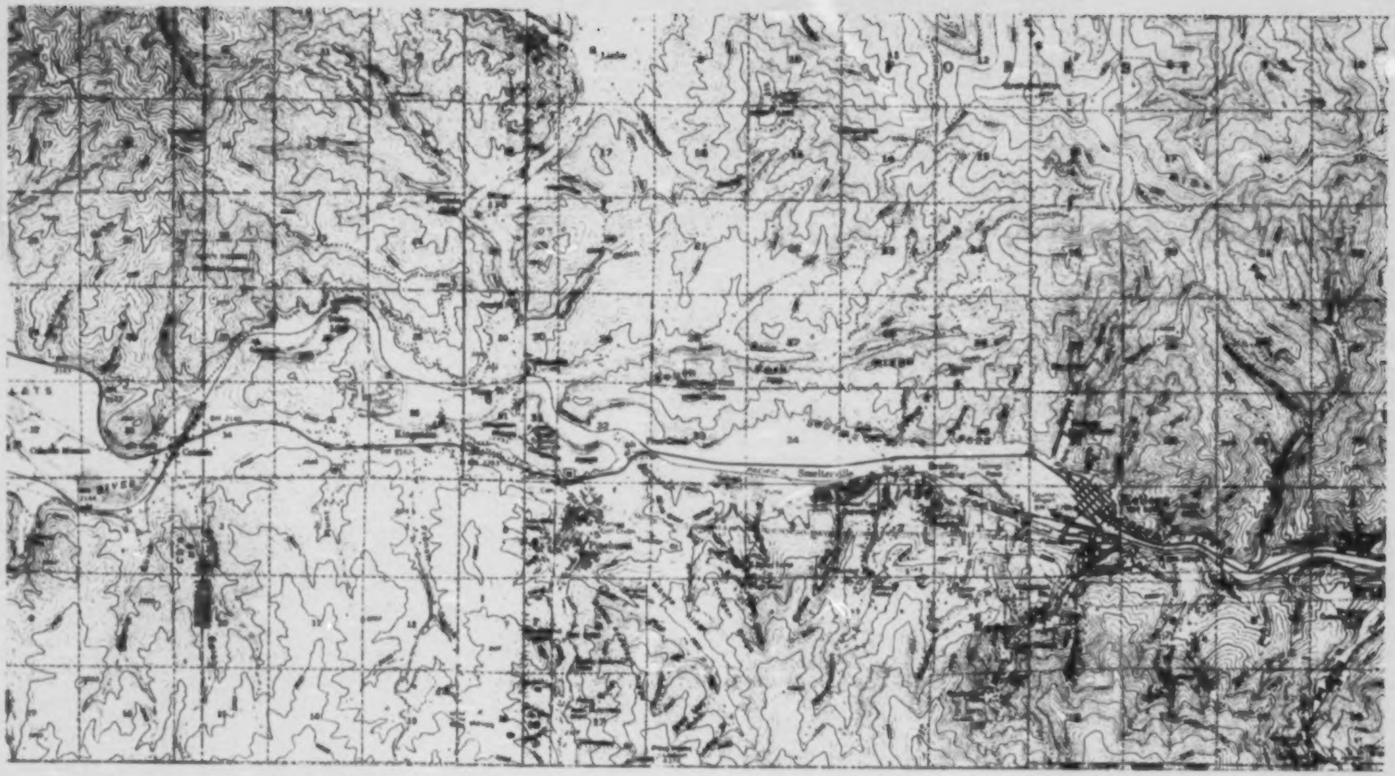

Figure 8 TOPOGRAPHIC MAP OF THE COEUR D'ALENE - KELLOGG AREA

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Table 14.

Bunker Hill et al. - Kellogg, Idaho - May 1973

THALLIUM concentration - ppm

Coeur d'Alene River	water	mud	algae	larvae and nymphs	fish
North Fork (control-clean)	<.0001	<.034	<.1 test	<.03	<.03
South Fork above outfalls at high school (control-sewage)	<.0001	<.037	0.043	none	none
tailings decant outfall	0.0014	<1.2	none	"	"
slag runoff in 1972	0.03 0.11	>15	0.28	"	"
raw granulating water	0.029	0.64 slag	none	"	"
Government Gulch at school	0.00018	0.12	none	"	"
South Fork at junction	0.0006	0.14	0.11	0.035	"

Table 15.

Bunker Hill et al - Kellogg, Idaho - May 1973
CADMIUM concentration - ppm

Coeur d'Alene River	water	mud	algae	larvae and nymphs	fish
North Fork (control-clean)	<.001	<2.6	1.2	<1.6	---
South Fork above outfalls at high school (control-sewage)	0.005	30	<5 test	none	none
tailings decant outfall	0.24	8.3	none	"	"
slag runoff in 1972	0.06	<2.4	254	"	"
raw granulating water	0.75-1 0.88	slag 270			
Government Gulch at school	1.4	280	none	"	"
South Fork at junction	0.017	59	36	2.9	"

Table 16.

Bunker Hill et al. - Kellogg, Idaho - May 1973

LEAD concentration - ppm

Coeur d'Alene River	water		mud	algae	larvae and nymphs	fish
North Fork (control-clean)	<.01		26	92	25	---
South Fork above outfalls at high school (control-sewage)	0.05		4100	26 test	none	none
tailings decant outfall	0.42		1800	none	"	"
slag runoff in 1972	0.04		310	111	"	"
raw granulating water	1.8 2	slag	7300			
Government Gulch at school	0.45		4300	none	"	"
South Fork at junction	0.045		4500	2700	680	"

Table 17.

Bunker Hill et al. - Kellogg, Idaho - May 1973

COPPER concentration - ppm

Coeur d'Alene River	water	mud	algae	larvae and nymphs	fish
North Fork (control-clean)	0.008	8	7.5	13	--
South Fork above outfalls at high school (control-sewage)	0.015	170	28 test	none	none
tailings decant outfall	0.26	3200	none	"	"
slag runoff in 1972	0.018	420	200	"	"
raw granulating water	0.03 0.05	slag 620			
Government Gulch at school	0.045	320	none	"	"
South Fork at junction	0.01	190	59	62	"

Table 18.

Bunker Hill et al - Kellogg, Idaho - May 1973

ZINC concentration - ppm

Coeur d'Alene River	water	mud	algae	larvae and nymphs	fish
North Ford (control-clean)	0.1	79	140	110	--
South Fork above outfalls at high school (control-sewage)	1.1	4900	200 test	none	none
tailing decant outfall	160	5200	none	"	"
slag runoff in 1972	0.072	12000	6900	"	"
raw granulating water	5	slag 20000			
Government Gulch at school	72	22000	none	"	"
South Fork at junction	1.8	4700	2200	350	"

Table 19.

Bunker Hill et al. - Kellogg, Idaho - May 1973

INDIUM concentration - ppm

Coeur d'Alene River	water	mud	algae	larvae and nymphs	fish
North Fork (control-clean)	<.1	1.5	2	0.4	3
South Fork above outfalls at high school (control-sewage)	<.1	4.1	3	none	none
tailings decant outfall	0.2	---	none	"	"
slag runoff in 1972	<.1	19.5	7	"	"
raw granulating water	<.1	slag 19			
Government Gulch at school		7.8	none	"	"
South Fork at junction	<.1	6.7	1.4	0.3	"

"Maggots" are aquatic larval diptera (crane flies).

Grass roots in river bed are probably annual.

Control larvae are ephemerid.

Mud below copper smelter slag was dry.

Control algae is probably Spirogyra.

The Sunshine mine produces the most silver and antimony in the U.S. Four others in the district including the Bunker Hill are third through sixth in lead and zinc production.

All outfalls and the larger dumps were sampled. The main Bunker Hill outfall on the river just below Kellogg High School was mostly acid (pH 2.2) and contained definite indications of Tl on preliminary analysis, as did Government Gulch below the acid plant and zinc refinery. A site at the mouth of the South Fork (junction of the N & S Forks) of the Coeur D' Alene River yielded an impoverished fauna. However, it was possible to obtain samples of beetles, a mixed sample of mayfly nymphs and cranefly larvae, as well as a sample of algae. The South Fork at Smelterville has an average discharge of 377 cubic feet/second (cfs) as measured by the U. S. Geological Survey. Its maximum flood in only 3 years of record was 2940 cfs. The North Fork of the Coeur D'Alene, however, drains relatively unpolluted terrain. Some old mine and placer dredge tailings in Prichard Creek, 24 miles above the junction, extend up to the ghost town of Raven. A relatively clean site was chosen three miles above the junction as control. Separate collections of may-fly nymphs, the stonefly Perlesta, water striders and cranefly larvae were made. Also a freshwater sculpin was taken for whole-body analysis.

In samples collected in September 1972, the acidic effluent* at the lead smelter was found to contain 0.02 ppm Tl and the mud washed off the large slag pile* along the south fork of the Coeur D'Alene River was found to contain more than 15 ppm Tl. Mink, Williams and Wallace (1971) found lead, cadmium, zinc, copper, nickel and iron in the river as a result of sulfide extraction. In addition, thallium has been found in Government Gulch particulates (1.5 ppm) and mud (0.4 ppm) below the Bunker Hill zinc plant. Both of these sources drain into the river where the mud at the junction of the forks is now found to contain 5 ppm of Tl.

The problem at Kellogg is still far from solved although diversion of Government Gulch wastes into the tailings pond will help. Until the slag is contained and enough quick lime or alkali is added, toxic metals will continue to enter the Coeur D'Alene River and, thereby, the Spokane water supply (now above Public Health Drinking Water Standards for Cu and Zn).

The data in Tables 14 through 19 are believed to be a fair illustration of the hazard.

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*Photographs can be found in Figures 9 and 10.

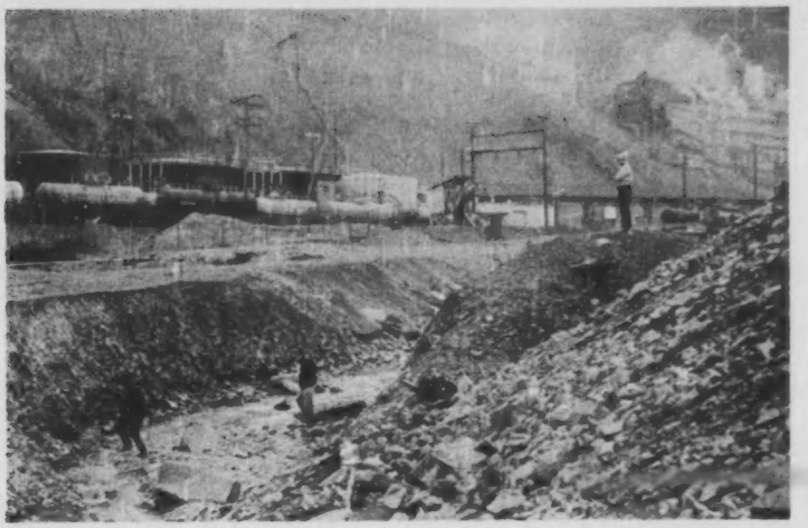


Figure 9 ACIDIC EFFLUENT AT ZINC REFINERY

Figure 10 SLAG PILE ALONG SOUTH FORK

East Helena, Montana

The ASARCO (American Smelting and Refining Co.) zinc smelter on Prickly Pear Creek includes a recently-closed lead smelter and Anaconda slag-fuming operation. It is processing 30% sulfur ore from the Texas Gulf Sulfur mine at Timmins, Ontario. The map in Figures 11 and 12 shows the location of the ASARCO smelter at East Helena, Montana, and the sites at which samples were collected. The creek is dammed by acres of slag being poured to a height of over a hundred feet. The hot-water stream running under the slag heap yielded only blue-green algae (Figure 13).

The creek was first sampled in September, 1972, and then on April 30, 1973. The 78°F water which comes from the cooling pond after washing the arsenical speiss ($Zn_3 As_2$), contained plant sewage. No improvements were made in the arrangement of outfalls or wastes between sampling periods.

Just above where the outfall re-entered Prickly Pear Creek, an abundant biota was found. The dragon fly nymph *Gomphus* occurred in small numbers. Caddis larva of the family *Hydropsychidae*, the stonefly nymphs *Perlinella*, *Isoperla* and *Pteronarcella* were large and abundant. These were all included in a collection of mixed benthos for analysis. Water striders made a separate sample. A similar collection was made in two locations above the smelter pond. The upstream biota is typical of a clean Rocky Mountain trout stream, even though the stream drains the placer gravels of Montana City. Additional upstream control samples were obtained on Prickly Pear Creek where it runs between old placer gravels in 6' high piles and a new paved highway. The new sampling point was located below the new Kaiser cement plant at Indiana, Montana, and above the East Helena smelter. However, fallout from the smelter stacks could have influenced the sample at this point.

An additional downstream sample was taken at the first major irrigation weir below the smelter and town to obtain more invertebrates. Here, the raw sewage from the smelter and town has a more immediate, apparent effect on biological productivity than does heavy-metal pollution.

Data on cadmium and lead found in samples acquired during our initial trip to East Helena are presented in Tables 20 and 21. Uncertainties above the detection limit are roughly 10% of the reported value. The septic sediment in oozes from East Helena showed 8.6 ppm thallium (Table 22).

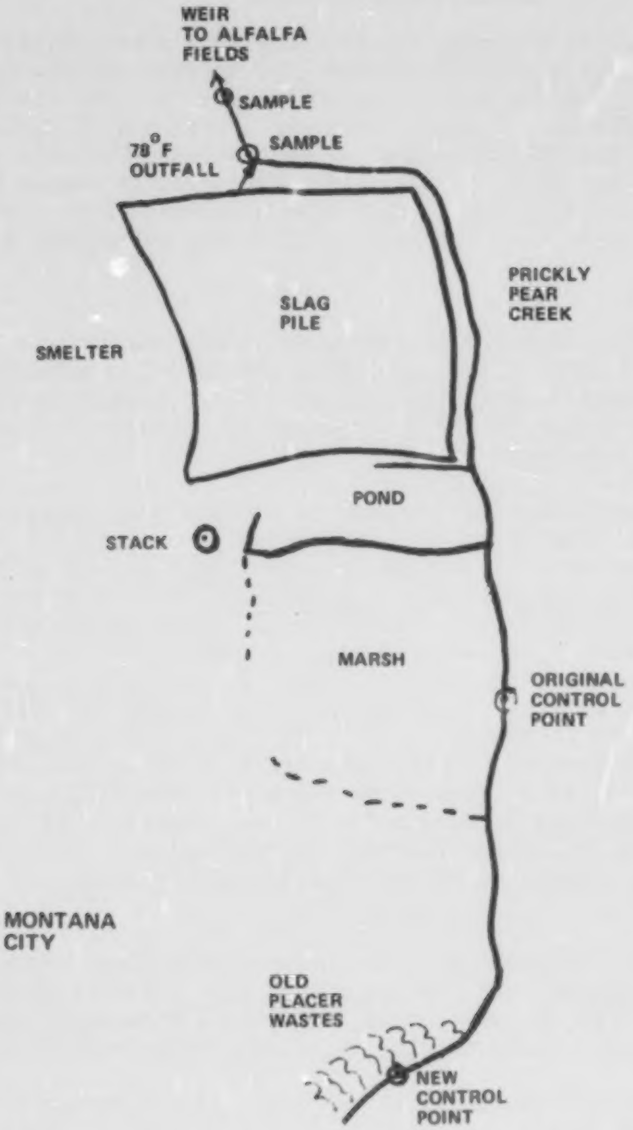


Figure 11 SKETCH OF ZINC (AND FORMERLY LEAD) SMELTER ASARCO – EAST HELENA

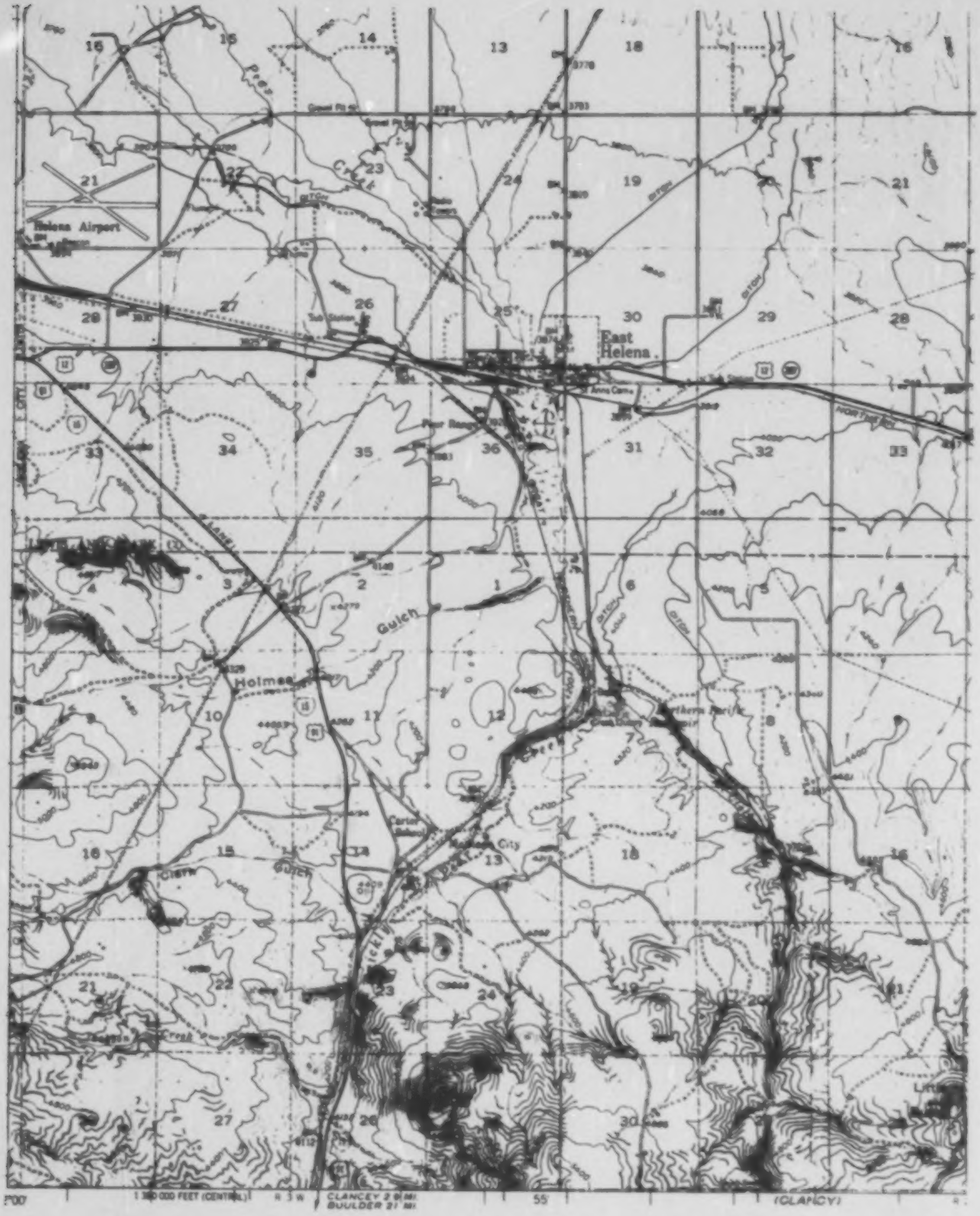


Figure 12 TOPOGRAPHIC MAP OF EAST HELENA AREA

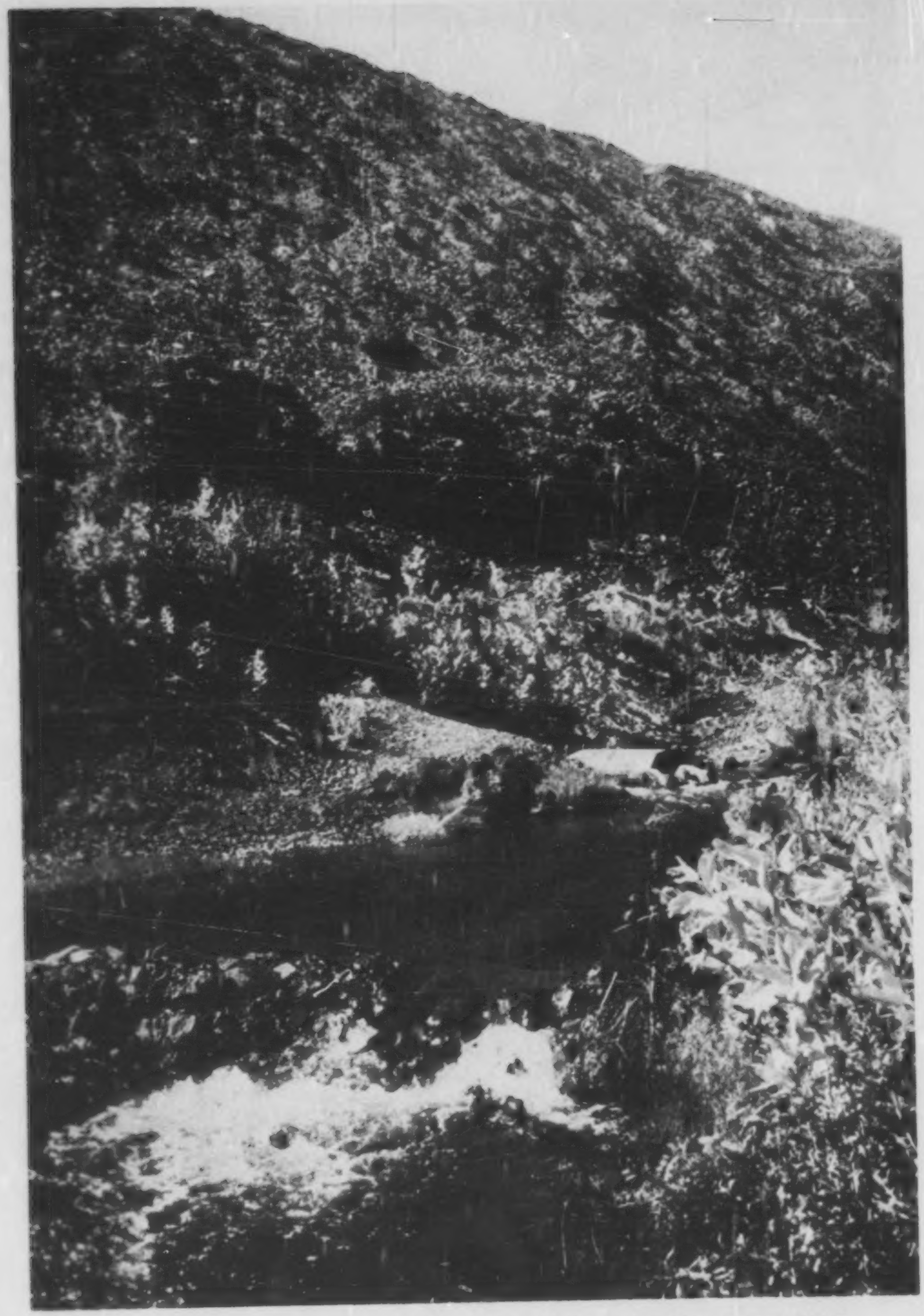


Figure 13 HOT WATER STREAM RUNNING UNDER SLAG PILE

Table 20.

EAST HELENA -- CADMIUM CONCENTRATION -- ppm

SAMPLING LOCATION	WATER	MUD	LEAVES*	ROOTS*	ALGAE	LARVAE	WATER STRIDERS	FISH
CONTROL#	< 0.002	3.4	0.88	10	1.5-1.8 (Spirogyra)	26-390 (mixed)	4.2	6.3 (sculpin)
POTENTIAL SOURCES:								
78°F SMELTER OUTFALL	.047	1500	--	--	86 (Cyanophyte)	270 (caddis)	--	none
DOWNSTREAM	< 0.002	170	--	--	200	10	31-74	none

* PERENNIAL RUSHES AND REEDS

# BELOW OLD PLACER MINING WASTES, POSSIBLY ALSO CONTAMINATED BY BACKWATER AND STACK DUST FROM SMELTER -- MORE DISTANT CONTROL SAMPLES TAKEN.

## Cottus bairdi

Table 21.

EAST HELENA -- LEAD CONCENTRATION -- ppm

SAMPLING LOCATION	WATER	MUD	LEAVES*	ROOTS*	ALGAE	SLIME**	LARVAE	WATER STRIDERS	FISH
CONTROL#	0.1	50,000	22	460	6.5 (Spirogyra)	40	79	76	34 (sculpin)
POTENTIAL SOURCES:									
78°F SMELTER OUTFALL	0.4	180,000	--	--	1100 (Cyanophyte)	--	1500 (caddis)	--	none
DOWNSTREAM	0.065	8,000	--	1400 (willow)	40-3700	--	330 (dragonfly)	550	none

* PERENNIAL RUSHES AND REEDS

** DIATOMS ON SPIROGYRA

# BELOW OLD PLACER MINING WASTES, POSSIBLY ALSO CONTAMINATED BY BACKWATER AND STACK DUST FROM SMELTER -- MORE DISTANT CONTROL SAMPLES TAKEN.

(Moth found on bank contains 1200 ppm)

Table 22.

EAST HELENA -- THALLIUM CONCENTRATION -- ppm

SAMPLING LOCATION	SLAG	MUD	LEAVES*	ROOTS*	ALGAE	SLIME**	LARVAE	FISH
CONTROL#			.063		< .052 (Spirogyra)	.012		<0.12 (sculpin)
POTENTIAL SOURCES:								
78°F SMELTER OUTFALL		8.6		1.0	.49 (Cyanophyte)		None	None
SLAG	low (being rereun)							
DOWNSTREAM					<.85		<.007 (Dragonfly)	None

*PERENNIAL RUSHES AND REEDS

**DIATOMS ON SPIROGYRA

BELOW OLD PLACER MINING WASTES, POSSIBLY ALSO CONTAMINATED BY BOCKWATER AND STOCK DUST FROM SMELTER--MORE DISTANT CONTROL SAMPLES WILL BE TAKEN.

Butte-Anaconda, Montana

The copper deposits of the Butte district (Figures 14 and 15) are examples of copper mineralization in the form of a great complex of veins. Over 7 million tons of copper metal have been mined from an area only 2.5 miles wide, 5 miles long, and about three-fourths of a mile deep. In addition, considerable amounts of silver, gold, zinc, and lead, along with some manganese have also been produced.

The host rock is a portion of the granodiorite Boulder batholith near its western border. Porphyry dikes intrude the host rock and are in turn cut by seven systems of faults. The ore deposits occur as steeply inclined veins deposited in these fault systems. They vary in width from a few feet to a few tons of feet and may persist as far as 7,000 feet in length. Each later fault system cuts and offsets the earlier.

The oldest fissures, termed the Anaconda, trend easterly and dip steeply south. They are long and wide, and persist at depth. These veins are rich and rather continuously mineralized, and they have been the great producers at Butte. The Blue system strikes northwest and dips steeply southwest, and its members cut the Anaconda system. Their ore is characteristically discontinuous and confined to irregular bodies. A central zone carries copper ores; an intermediate zone contains copper and zinc ores; and an outer zone is dominated by zinc blende along with a little galena, chalcopyrite and silver, in a gangue of calcite, rhodochrosite, rhodonite and quartz. These ores yield zinc, manganese and silver. They are typical hydrothermal fissure veins in granodionite of the Boulder batholith. The principal copper minerals are chalcocite, enargite, bornite, chalcopyrite, tennantite, tetrahedrite, and covellite. The gangue minerals are mostly quartz and pyrite. The zinc sulfide, sphalerite, is abundant in certain zones, as is also the manganese carbonate, rhodochrosite.

East of the point where the Anaconda vein becomes discontinuous, mineralization is represented by a series of segments arranged en echelon. Ore in this area occurs in numerous veinlets striking northwest with a stockwork of connecting stringers, irregular lenses, and disseminations of copper-bearing sulfides. This intensely fractured "horsetail" area is about 2,000 feet long, from 300 to 500 feet wide, and extends down below the 3,400-foot level.

The vein systems and the "horsetail" zone contain identical ores that apparently were all formed during the same period of mineralization. The later systems are post-mineral faults that cut and displace the ore-bearing veins, giving rise to disconnected segments of the latter.

The Anaconda mill (Figures 14 and 15) at the headwaters of Silver Bow Creek processes the large volumes of ore from this pit. The new acid-leaching plant and other modern processing facilities discharge through a series of tanks and ponds into a reservoir in the creek valley with an elaborate floating wastewater facility.

At Butte (Table 23 and Figures 14 and 15), the Tl initially found in the acid Berkeley Mill effluent (headwaters of Silver Bow Creek) is also found in the crust and mud downstream in the abiotic creek (iron crust-10 ppm; mud-0.5 ppm; floodplain soil-0.6 ppm). No algae were found. Below Anaconda, pH is restored by the confluence of alkali smelter wastes with the acid discharge from the leaching plant in Butte.

Unlike Kellogg, the lower rainfall of Butte and Anaconda makes water rights of value and reuse desirable. Thus, the relative effluent volumes are small. In the first sampling period, pH values were low. Since that time, however, new water treatment facilities serve to reduce the heavy metal load and, hence, raise pH values.

Defense Smelter

The abandoned federal smelter on Silver Bow Creek is located just below downtown Butte. In constructing the interstate highway, the creek has been diverted through a new channel blasted in the old slag pile (Figure 16). The pH was so low (4.3) and metals were so concentrated that iron oxides, at least, were precipitating on solid wastes in the channel. Those materials which are being leached or eroded were sampled.

The Defense smelter (Figures 14 and 15) had been leased in 1973 by Anaconda and was used as a lime kiln during rebuilding of their kiln at the smelter. The milk of lime producedwas being added at the Berkeley Mill (Figure 17), rather than the old procedure (Figure 18) of allowing mill and smelter wastes to mix in the settling pond below Silver Bow Creek. Although some additional metal was discharged from the smelter, much less was leaving the mill during sampling in 1973. Tables 23-28 list the results of the analyses for the samples collected in May 1973. The temporary lime kiln effluent contained 5.5 ppb Tl in waste sediment, carried in the alkaline water.

There was a total absence of benthos all along Silver Bow Creek. However, some aquatic weeds were taken from Blacktail Creek, a tributary draining residential and commercial areas just above the Defense smelter. There are other abandoned plants and waste deposits in Butte and vicinity. All drain into abiotic Silver Bow Creek.

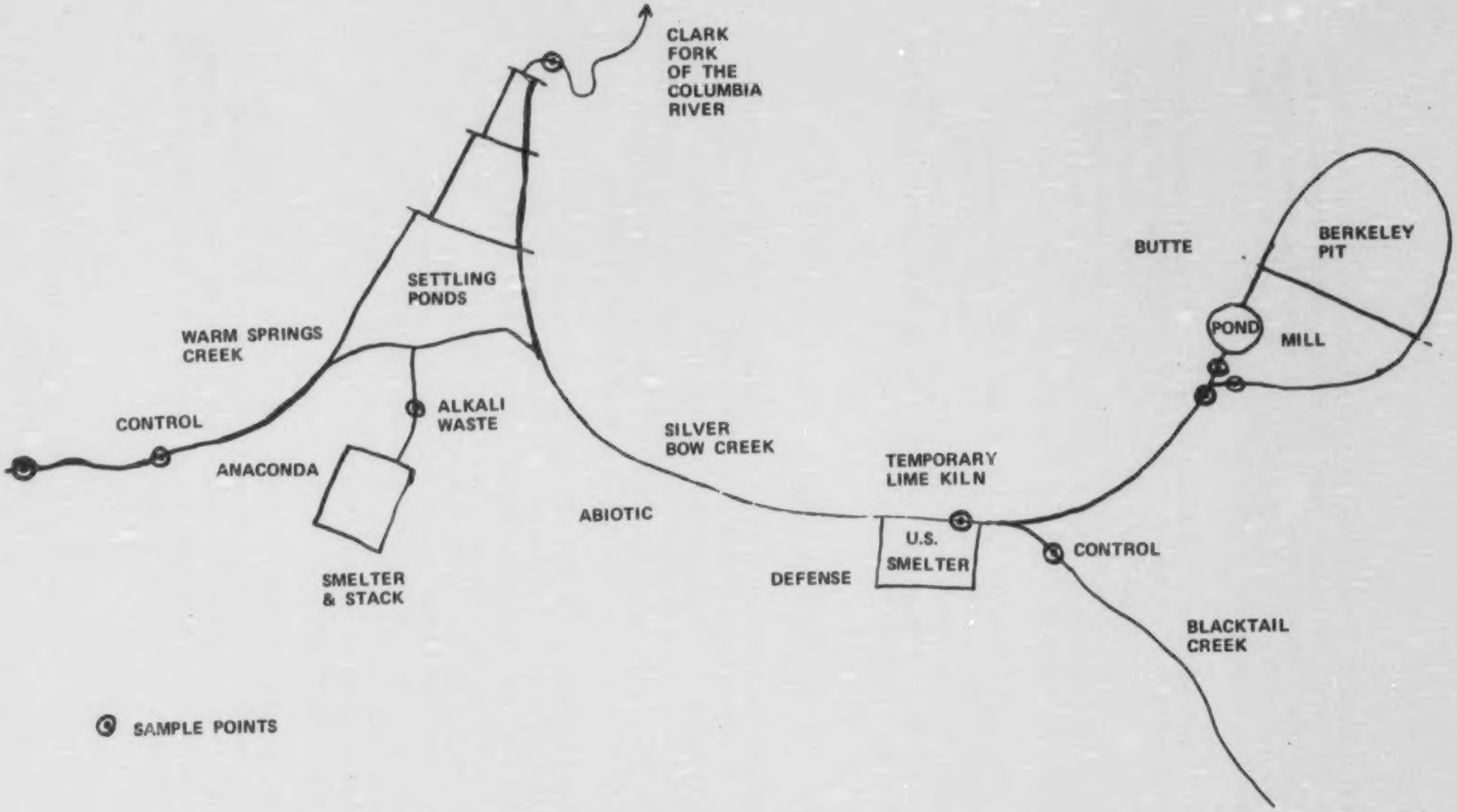
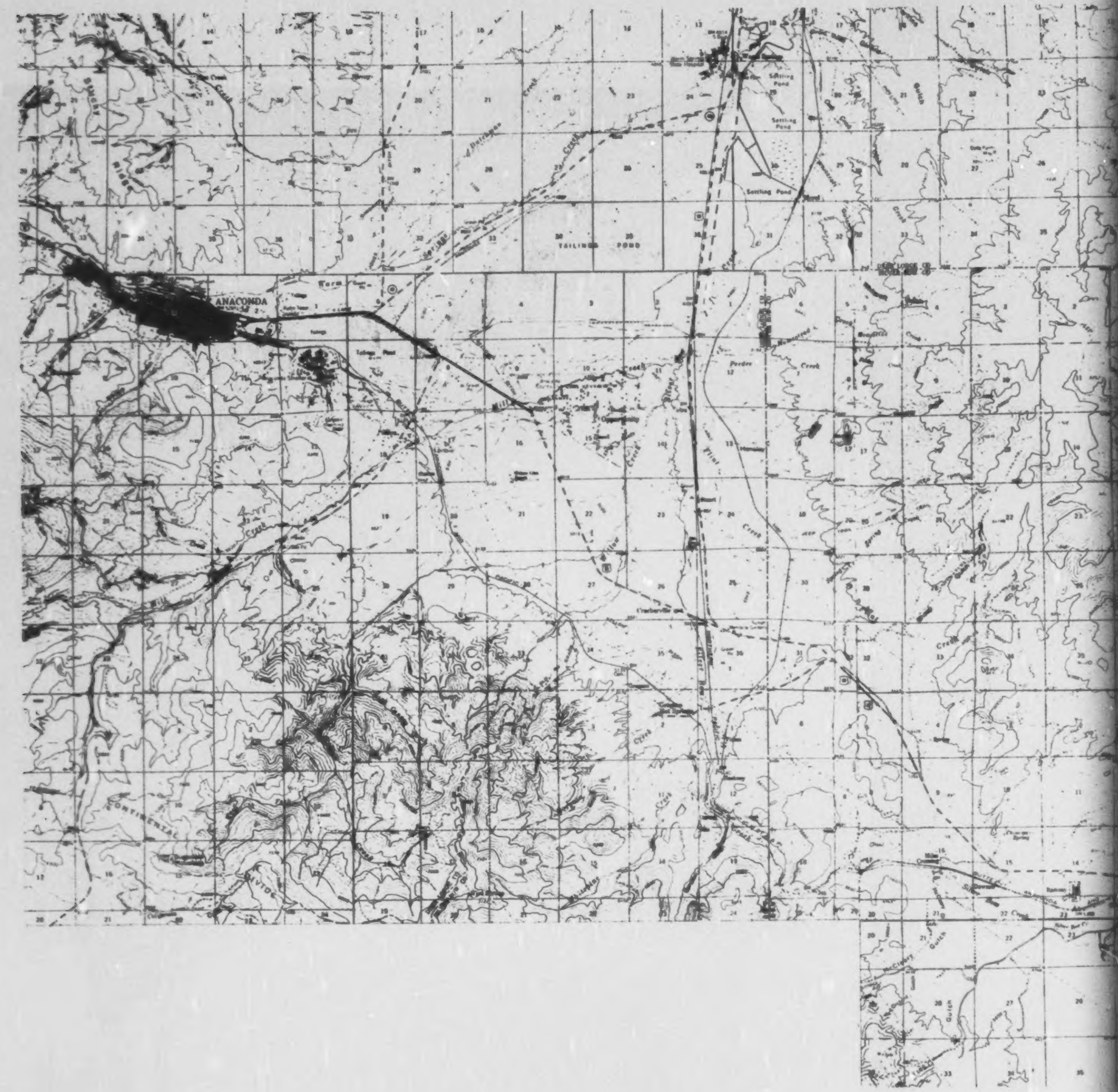


Figure 14 SKETCH OF ANACONDA CO. MONTANA COPPER OPERATIONS


ANACONDA
Settling Pond
Settling Pond
Settling Pond
TAILINGS POND
Warm
Mill
Creek
Creek
CONTINENTAL
DIVIDE

A

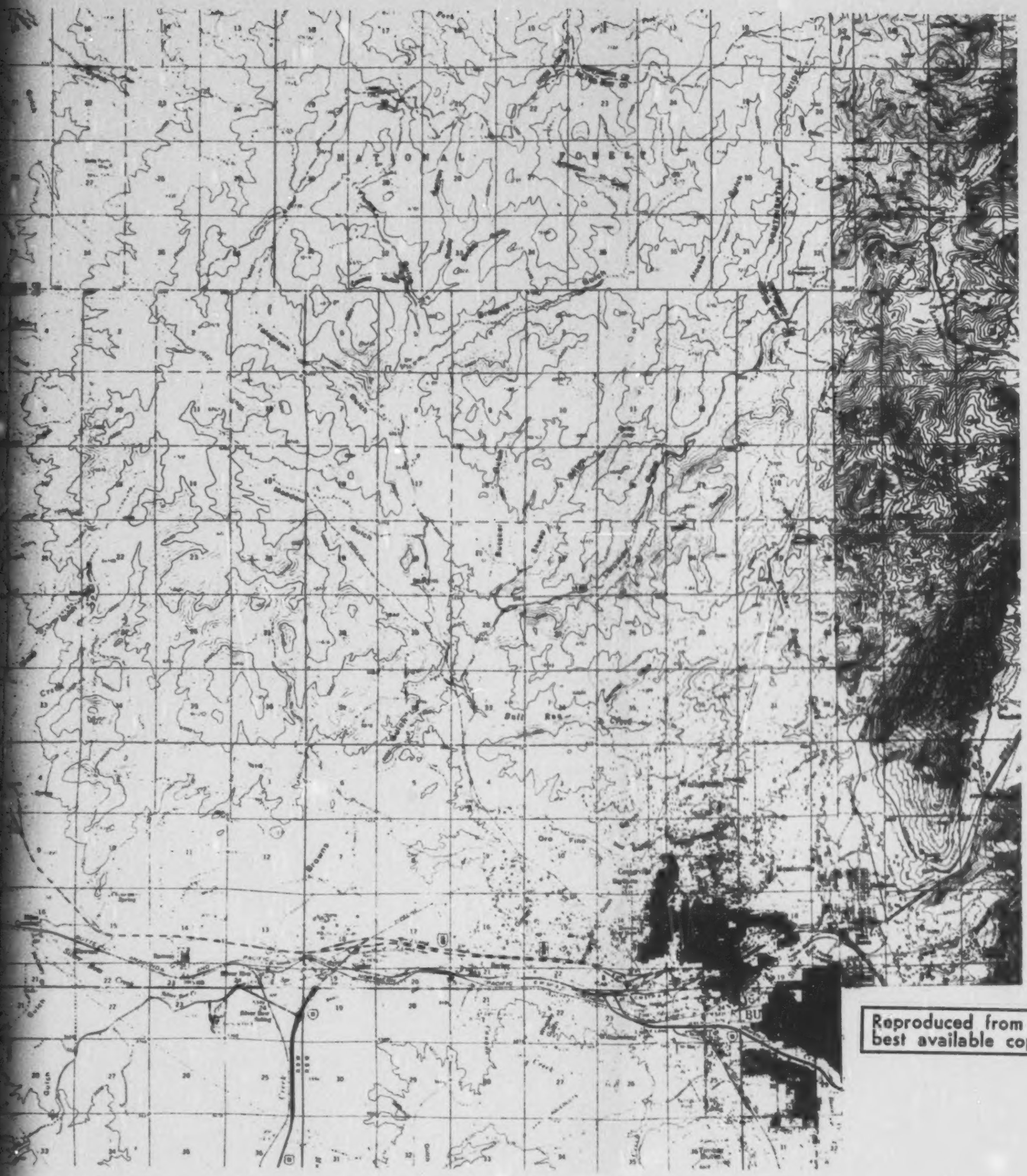


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Figure 15 TOPOGRAPHIC MAP OF ANACONDA, MONTANA AREA

β

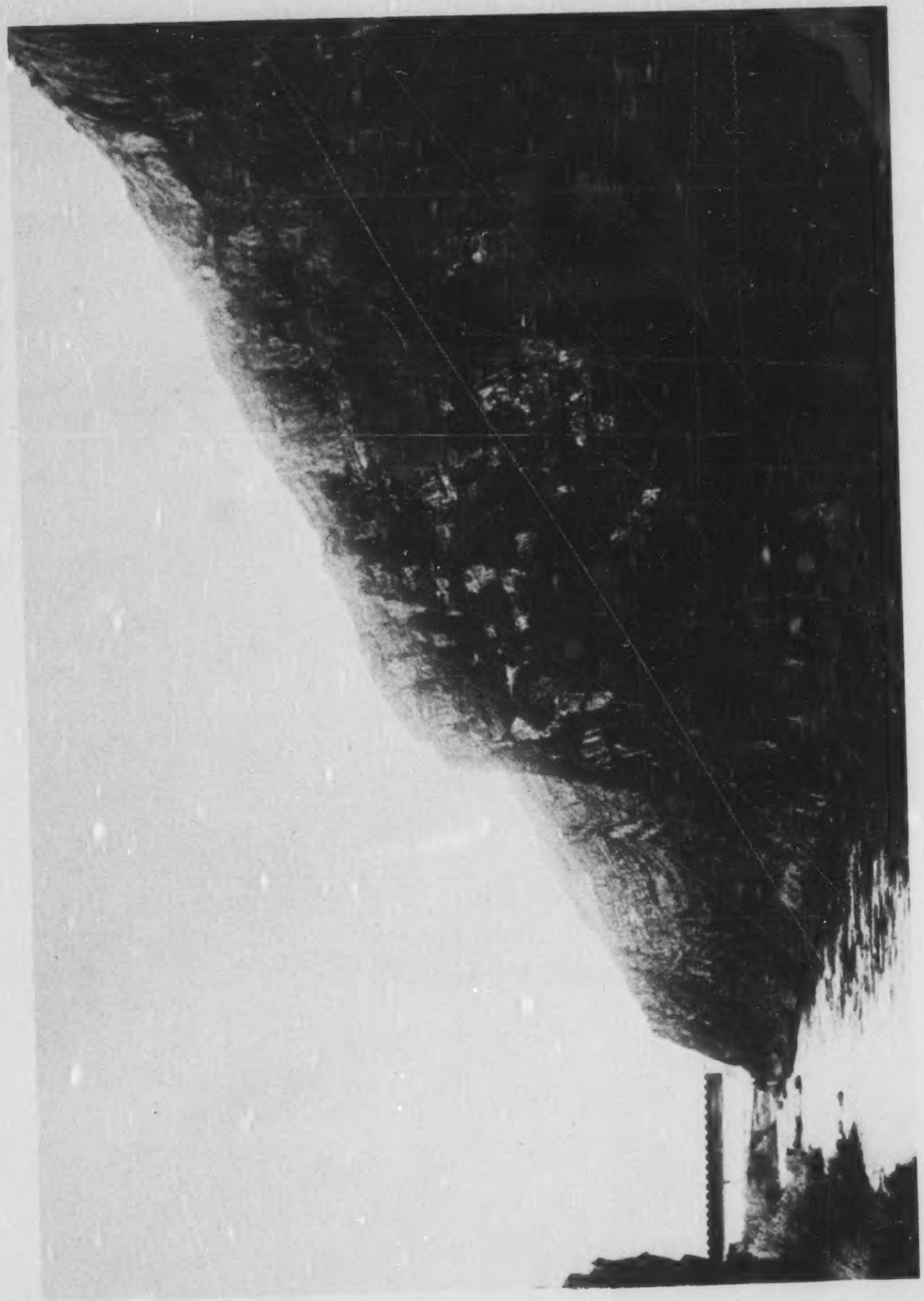

Figure 16 NEW STREAM CHANNEL BLASTED IN OLD SLAG PILE

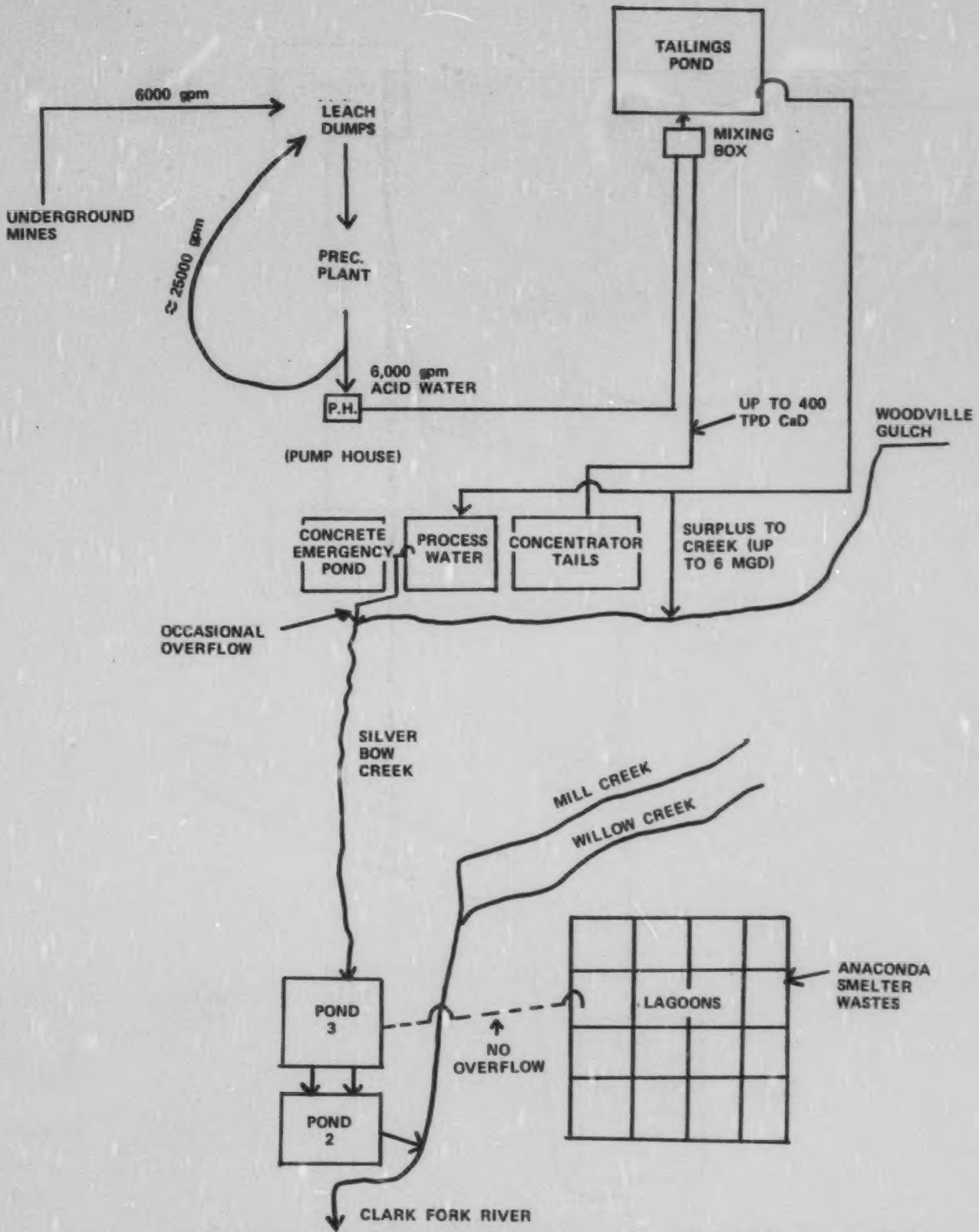

Figure 17 WASTEWATER TREATMENT SYSTEM, ANACONDA COMPANY, BUTTE, MONTANA COPPER OPERATIONS (MAY 1973)

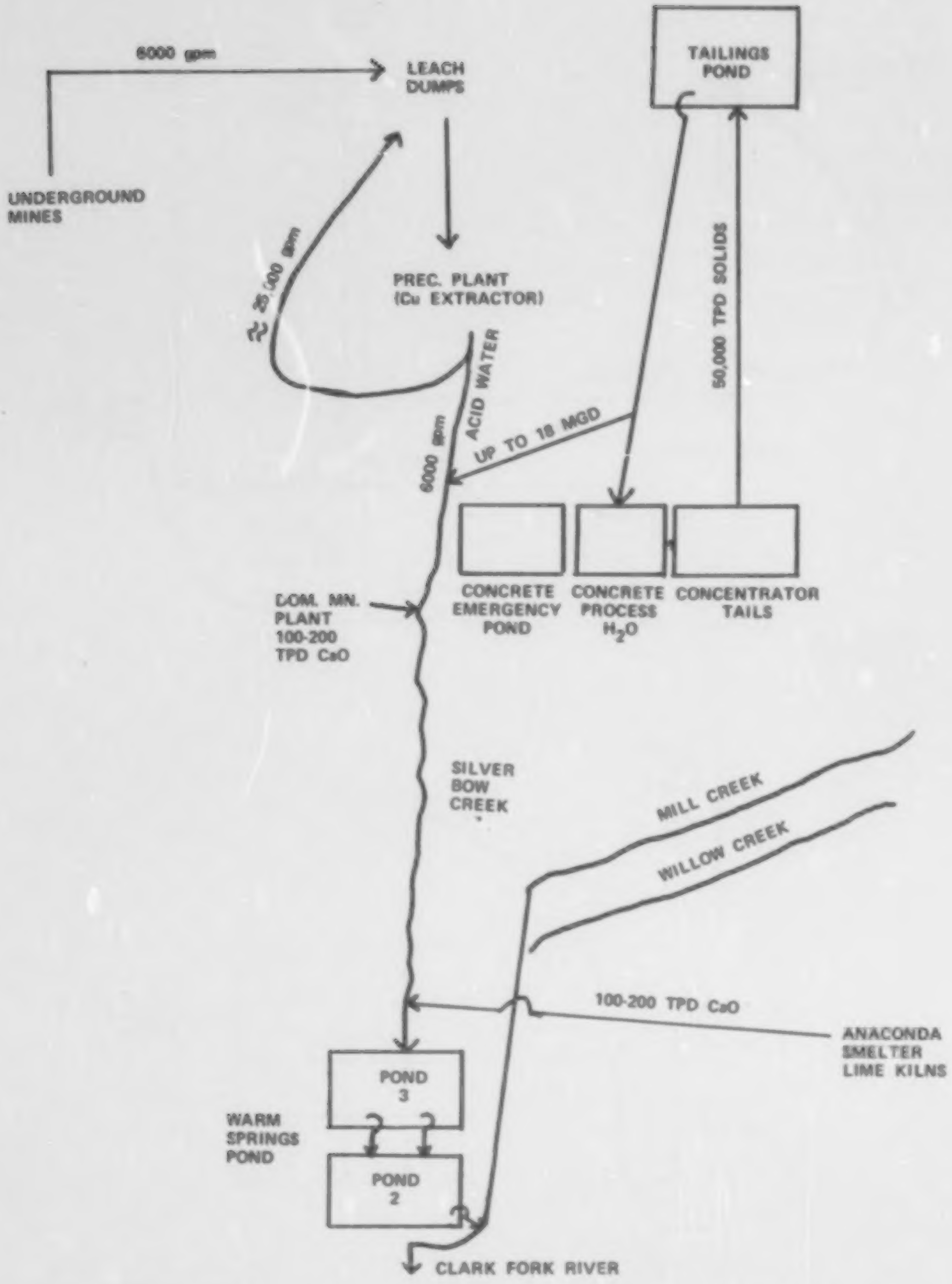

Figure 18 WASTEWATER TREATMENT SYSTEM PRIOR TO OCTOBER 1, 1972, ANACONDA COMPANY, BUTTE, MONTANA, COPPER OPERATIONS

TABLE 23.

1972

ANACONDA-BUTTE -- THALLIUM CONCENTRATION -- ppm

SAMPLING LOCATION	WATER	TAILINGS	CRUST	FLORA	LARVAE
CONTROL* (Blacktail Creek)	Not Detected			Aquatic Moss <.21 Aquatic Weeds <.084	Tipulid <.073
POTENTIAL SOURCES:					
MILL	0.2	0.52-.61	>10	Lifeless	
DOWNSTREAM	<0.01			Horsetails <.02	Too Few

* MOST UPSTREAM TRIBUTARY TO SILVER BOW CREEK

TABLE 23. (Cont'd)

THALLIUM concentration Anaconda-Butte May 1973
ppm

	pH	water	mud	algae	larvae and nymphs	sculpin
Warm Springs Creek above Anaconda	5.5	0.00025	<.02	<.02	0.003	0.004
mill	10.3	<.0001	<.04 (10 in 1972)	none	none	none
kiln	11.5	0.00055	muddy water	none	none	none
smelter	8.4	<.0001	0.04	none	none	none
Clark Fork below Warm Springs		0.00018	<.03	none	<.07	none

TABLE 24.

CADMIUM concentration
ppm

Anaconda-Butte May 1973

	Water	Mud	Algae	Larvae and Nymphs
Warm Springs Creek above Anaconda	0,002	2,8	3	1.3
mill	0,002	19.5	none	none
kiln	0.002	muddy water	"	"
smelter	0,001	2,5	"	"
Clark Fork below Warm Springs	0.004	3	"	<6.7

TABLE 25.

LEAD concentration
ppm

Anaconda-Butte

May 1973

	Water	Mud	Algae	Larvae and Nymphs
Warm Springs Creek above Anaconda	<.01	22	28	9-19
mill	<.01	111	none	none
kiln	0.03	muddy water	"	"
smelter	0.02	81	"	"
Clark Fork below Warm Springs	<.01	25	"	34

TABLE 26.

COPPER concentration ppm — Anaconda-Butte — May 1973

	Water	Mud	Algae	Larvae & Nymphs
Warm Springs Creek above Anaconda	0.022	63	<7	10-16
mill	0.030	3200	none	none
kiln	0.057	muddy water	"	"
smelter	0.06	1100	"	"
Clark Fork below Warm Springs	0.048	400	"	74

TABLE 27.

ZINC concentration Anaconda-Butte May 1973
ppm

	Water	Mud	Algae	Larvae and Nymphs
Warm Springs Creek above Anaconda	0.017	97	68	61-65
mill	0.023	2000	none	none
kiln	0.085	muddy water	"	"
smelter	0.11	1350	"	"
Clark Fork below Warm Springs	0.21	900	"	320

TABLE 28.

INDIUM concentration Anaconda-Butte May 1973
ppm

	Water	Mud	Algae	Larvae & Nymphs
Warm Springs Creek above Anaconda	<.1	2.5	1.1	0.4
mill	0.1	5.2	none	none
kiln	0.25	muddy water	"	"
smelter	<.1	6.4	"	"
Clark Fork below Warm Springs	<.1	5.3	"	<.7

Anaconda Smelter

The company smelter complex (Figures 14 and 15), the largest single copper source in the U.S., drains into Warm Springs Creek. The tailings ponds extend over six miles below the smelter to the headwaters of the Clark Fork River (formed by Warm Springs and Silver Bow Creek) covering at least four square miles. Calspan sampling covered these wastes and waters.

The Anaconda smelter is the only industry in the valley since a zinc smelter was closed in 1969. The large copper smelter reduced polymetallic-sulfide concentrates from the mill in Butte. The biota within five miles of the smelter was severely limited by heavy-metal and sulfur toxicity. Very old, hardy shrubs, *Tetrodynia* and *Chrysothamnus*, and a few cottonwoods and willows barely survive. Reedgrass (*Calamagrostis montanensis*) exists temporarily on clean, newly-eroded soil. No wild animals or mature insects can be found (Munshower, 1972). The wastewater handling facilities resemble those at the mill in Butte. Arsenic exposures are relatively high in Anaconda (Hammer et al., 1972).

The Clark Fork site sampled, receives acid wastes from the Butte mill which are partially neutralized by alkaline (pH 12.7) smelter effluent from the settling ponds (subject to winter overflow). This portion of the river is also contaminated by partially-treated sewage from the town and nearby state hospital.

An uncontaminated site on Warm Springs Creek above the town was sampled for control. A large species of the caddis larva family *Hydropsychidae* formed one collection. A giant stonefly nymph, *Peltoperla*, formed another collection. A collection of the caddis larva *Brachycentrus* were removed from their cases and stored for analysis. In the following spring collection, stoneflies included *Arcynopteryx*, *Pteronarcella* and *Perlinella*; mayflies included *Ephemerella*, *Arthroplea* and *Potamanthus*; caddisflies were *Hydropsychiad* and *Psychomyiid*.

Warm Springs Creek upstream from Anaconda contains 0.25 ppb Tl in the water. Although the drainage basin is now almost uninhabited grazing land, it contains old mine workings, dumps and many prospect pits in a locally complex volcanic terrain recently heavily glaciated.

Tl may be leaching out of both the old mining debris and glacial till. The large mayfly larvae contain 3 ppb Tl and a small sculpin contains 4 ppb Tl, showing a bioconcentration factor of 12-16 times the concentration in water. Smaller, rarer mayfly larvae collected at this site in the fall contained 200-240 ppb Tl. They have accumulated through the open-water season a bioconcentration factor of almost 1000. This contamination was reduced to less than 0.1 ppb above Anaconda as side gulches diluted it. The mine debris and glacial till leach cannot be the source of all the Tl still found in Clark Fork. At least 40 ppb Tl in mud was entering from the smelter due to low pH (Table 23). The other control stream, Blacktail Creek at Butte, shows no Tl.

For comparison, the Tl concentrations sampled in September 1972 from the Berkeley Mill at Butte were up to 0.2 ppm in the mill effluent water (pH 2.6), about 0.55 ppm in the mud (tailings) and over 10 ppm in the iron crust deposited in the stream bed. It is clear that the acid discharge from the mill carried more toxic heavy metals.

As an additional check, Silver Bow Creek was sampled between the mill outfall and the junction of Blacktail Creek at George and Kaw Streets. The analysis closely confirms the data from the mill outfall for all metals in both water and mud.

Basin, Montana*

A typical small smelter and mill ruins on the Boulder River were used to process local ore in the last century. Structural collapse allowed collection of flue and grinding dusts from hot locations which are inaccessible in a functioning plant. Slags have been removed and reworked for their metal values. Samples were taken of the large tailings dump along the river, its leachates and the river water. The river now has a pH of 8.7. Solid wastes contain as much as 5.1% zinc, 1.0% copper, 0.79%lead, 420 ppm cadmium and 440 ppb thallium. No biota was found. Only 8 ppb of copper was found in the water. Many such small abandoned plants can be found throughout the western mining districts. Containment of their accumulated wastes would be relatively inexpensive in each case if necessary.

Southwest Area

Copper mining, milling and smelter operations in the Southwest were sampled from the Colorado River to the Rio Grande. In this arid region, water is expensive. Most facilities store and recycle

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*Figure 19 is a topographic map of the area.

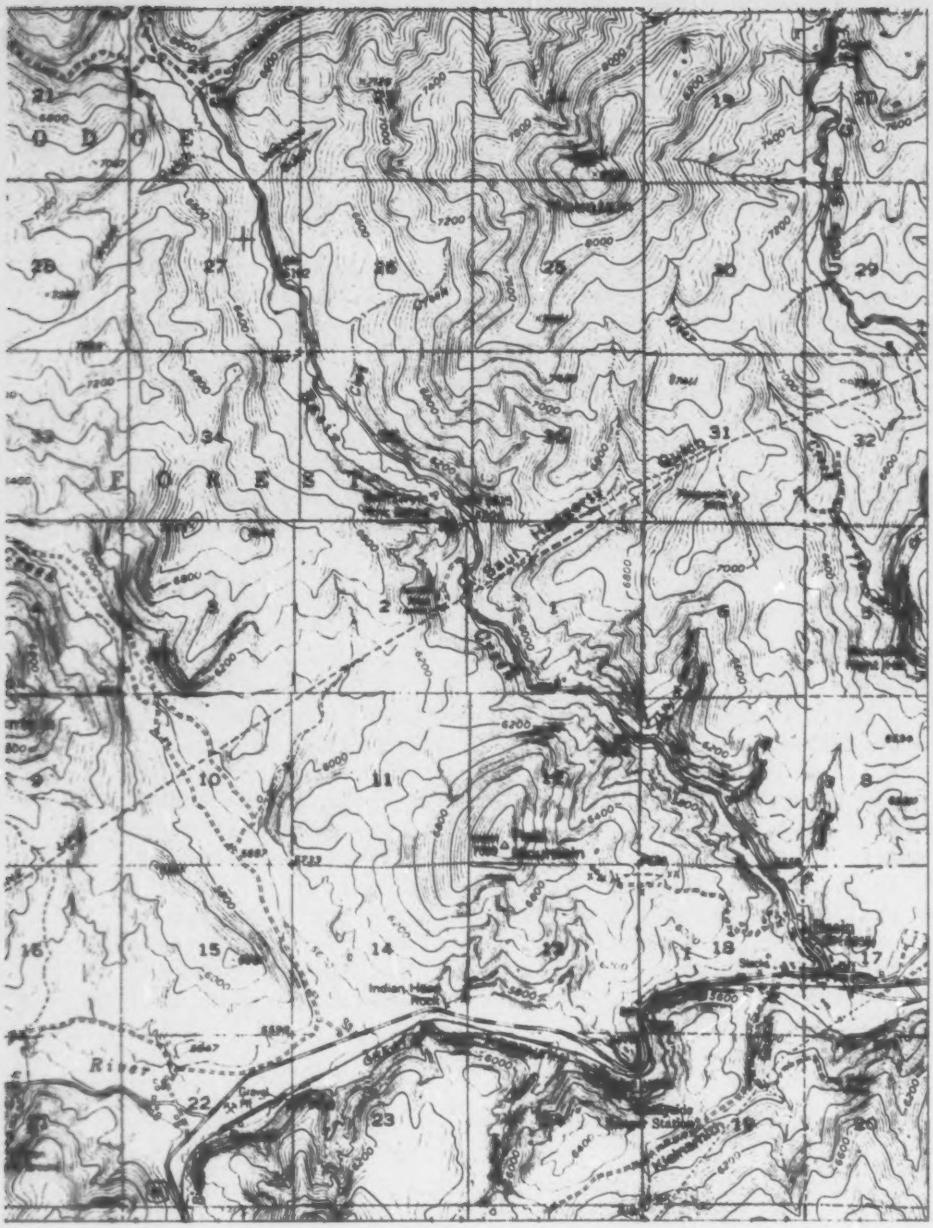

Figure 19 TOPOGRAPHIC MAP OF THE BASIN, MONTANA AREA

all of the water, including rainfall, which falls on the mine, tailings or slag and runoff. Results of sampling in January 1973 from the copper processing plants in this area are discussed below.

Porphyry District, Arizona

The Arizona porphyry copper mining district, which supplies most of the Cu today, is in a very dry climate with few permanent streams. The centrally-located smelters and acid plants at Hayden, however, are directly on the Gila River, which is one of the principal sources of irrigation water for Arizona agriculture.

The Ajo, Douglas, Duval and other mines in the porphyry belt south of Tucson have no surface runoff to ocean or irrigation.

The porphyry district is underlain by the late-pre-Cambrian sediments found in Montana and Idaho. This thick series includes the Pinal schist, a metamorphosed cupriferous blackshale which can be correlated with the ore at White Pine, Michigan. The copper was mobilized by hot igneous intrusions and crystallized in the partially-quenched (200-300°C) rim of large ivory-colored oligoclase feldspar ($NaAlSi_3O_8$ with 10 to 30% $CaAl_2Si_2O_8$) crystals in a purple ground-mass of fine-grained minerals. The overlying Paleozoic limestone trapped the richest ore bodies (skarns) where they were cut by porphyry stocks, particularly immediately below shales.

Phelps Dodge operations at both Morenci, Arizona and Tyrone, New Mexico, are so combined that water is fully recycled. Location of facilities is partially controlled by access to water.

Kennecott at both Ray-Hayden, Arizona, and Chino-Hurley, New Mexico, still uses a mill at the smelter rather than close to the mine.

Hayden and Vicinity, Arizona

Sampling locations in the Hayden-Ray vicinity, Arizona are shown in Figures 20 and 21. On the west side of the Pinal Mountains, the Magma Copper Co. at Superior permanently transferred smelting operations to Mammoth during a strike in 1970. In the original Magma mine, still operating up the mountain above the mill and closed smelter,

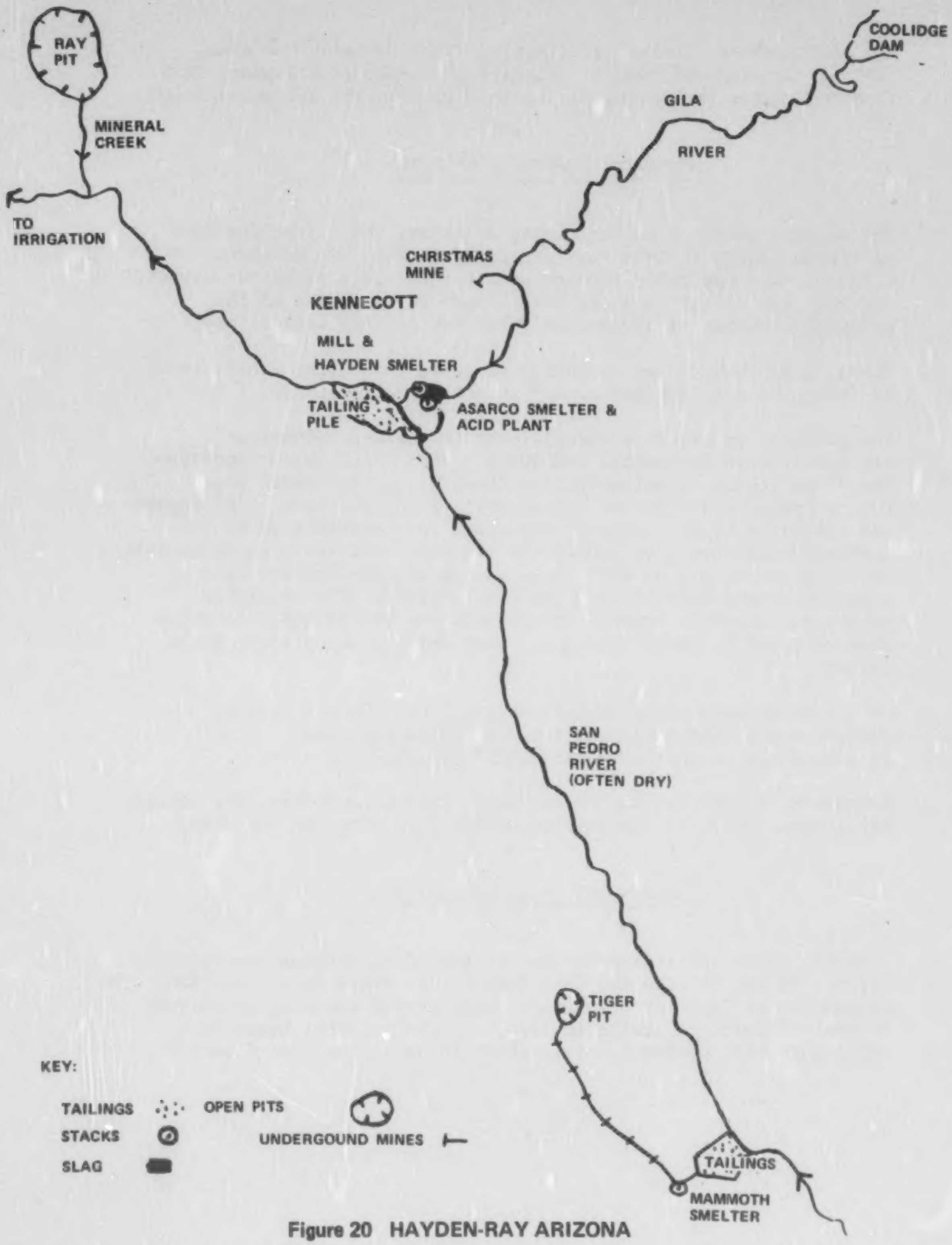

Figure 20 HAYDEN-RAY ARIZONA

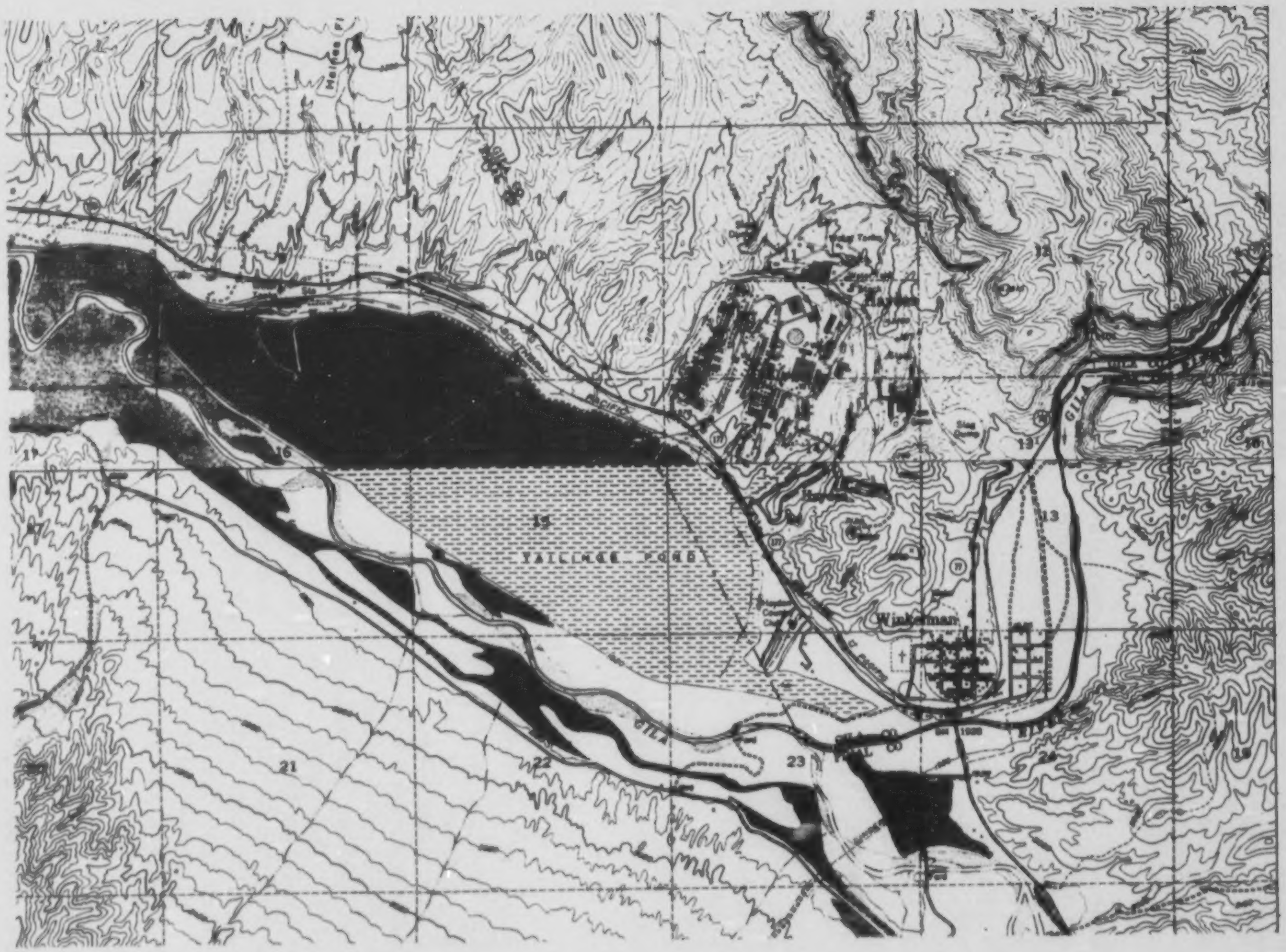

Figure 21 TOPOGRAPHIC MAP OF THE HAYDEN-RAY, ARIZONA AREA

the mineral relations of porphyry copper have been worked out in greatest detail. The hot cupriferous water flowed along shear zones to deposit massive sulfides in the thin coralline Martin limestone (Devonian Onondaga equivalent). Analyses of water, sediment and cattails from this old mining area are given in Tables 29-31.

The Kennecott Ray pit, almost two miles across, is in a large blanket ore deposit in the Pinal schist drained by Mineral Creek (sampled below the acid leach plant and at Kelvin where it joins the Gila River).* Only the Kennecott pit at Ray, Arizona, has a large runoff problem, which will eventually be corrected by a long diversion tunnel. All of the facilities whose runoff could enter surface irrigation or domestic supplies were sampled. The creek ran copper-blue. It is abiotic below the mine as was the Gila River below its confluence. There was no recycling and this stream provided most of the water for citrus and lettuce irrigation below Florence at low flow. Biota were collected above Mineral Creek and above the mill-smelter outfall at Hayden. The Kennecott Hayden mill-smelter complex recycle system was incomplete. Runoff water precipitated metal deposits in Hayden (sampled). It drained from a tailings pond second in size only to Anaconda. The ASARCO smelter and acid plant recycle all water but cause heavy fumes down the Gila Valley. Results of thallium, cadmium and lead analyses in water sediments, and algae are given in Tables 32-34.

Globe-Miami, Arizona

The layout of the Globe-Miami area is shown in Figures 23 and 24. The middle of the mountain range is occupied by barren, coarse Schulze granite. On the east side, the 2-1/2 mile-long Miami-Inspiration lode forms a rim around a lobe of porphyry. The Inspiration smelter sits on a 250-foot high pinnacle of ore surrounded by wind-blown tailings and slag (sampled). The water from the smelter and mill was recycled through the acid-leach (sampled). The Inspiration facilities, the Bluebird mill (sampled) in Bloody Tanks Wash (control samples above Bloody Tanks), the ruined smelter in Globe (slag sampled), and the CITGO (Cities Service) and AMAX (American Metals Climax molybdenum) operations up Tinhorn Wash drain into dry Pinal Creek, a tributary of the Salt River, which was sampled below Radium. Analyses of water, sediments and biota are given in Tables 35 and 36.

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*Figure 22 shows a photo of Mineral Creek at the acid leach plant where samples were taken.

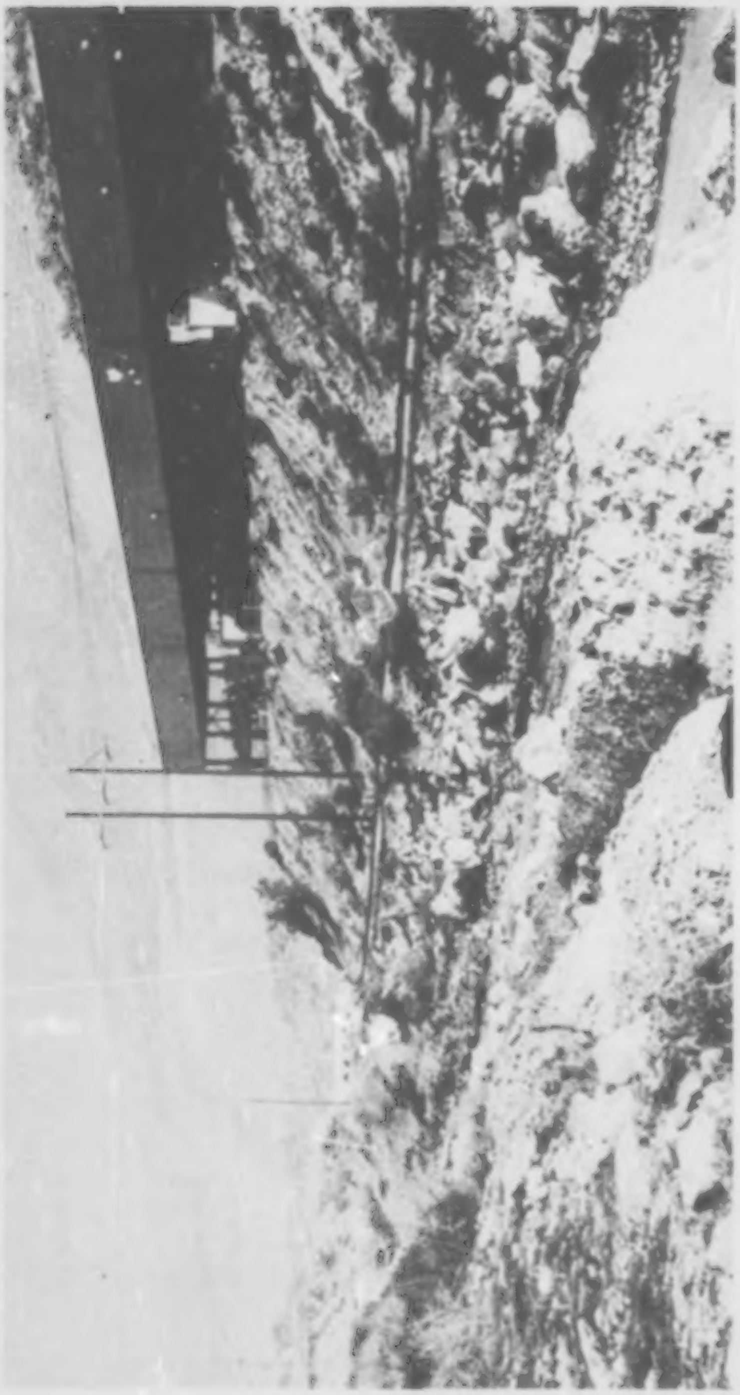

Figure 22 MINERAL CREEK AT THE ACID LEACH PLANT

TABLE 29.

THALLIUM - ppm

Magma Copper Co., Superior, Arizona

	water	sediment
Queen Creek draining mine	0.003	0.11
old mill (closed)	0.0033	0.089

TABLE 30.

LEAD - ppm

Magma Copper Co., Superior, Arizona

	water	sediment	cattails in pond
Queen Creek draining mine	<0.01	16600	none
ore	none	28400	"
old mill (closed)	<0.01	1200	16.7
old smelter (closed)	<0.01	1870	none

TABLE 31.

CADMIUM - ppm

Magma Copper Co., Superior, Arizona

	water	sediment	cattails
Queen Creek draining mine	<0.0005	2.6	none
ore	none	1.9	"
old mill (closed)	0.0005	1.8	0.05
old smelter (closed)	0.0045	0.62	none

TABLE 32.

Thallium - ppm

Kennecott, Ray-Hayden, Arizona

	water	sediment	algae
Gila River			
above Hayden (below Christmas mine)	<0.003	0.22	0.36
Hayden concentrator	< 0.003	0.12	nothing alive
smelter	< 0.003	0.16	" "
Ray pit	drains into Mineral Creek	0.11 - 0.15	" "
Mineral Creek	0.004 - 0.005	0.12	" "
Gila River below junction	<0.003	<0.11	" "

TABLE 33.

LEAD - ppm

Kennecott, Ray-Hayden, Arizona

	water	sediment	algae	caddis & blackfly larvae
Gila River above Hayden	<0.005	85	125-260	900
Hayden				
concentration	<0.01	2140	nothing alive	nothing alive
smelter	<0.01	23200	" "	" "
Ray pit	drains into Mineral Creek	8200-9400	" "	" "
Mineral Creek	0.01	1240-1320	" "	" "
Gila River below junction	0.015	1120	" "	" "

TABLE 34.

CADMIUM - ppm

Kennecott, Ray-Hayden, Arizona

	water	sediment	algae	fish
Gila River above Hayden	<.0005	0.63	0.75	2
Hayden				
concentration	0.002	1-1.2	nothing	alive
smelter	0.0005	0.9-1.2	"	"
Ray pit	draws into Mineral Creek	2.4	"	"
Mineral Creek	0.048	0.3-0.35	"	"
Gila River below junction	0.017	0.45	"	"

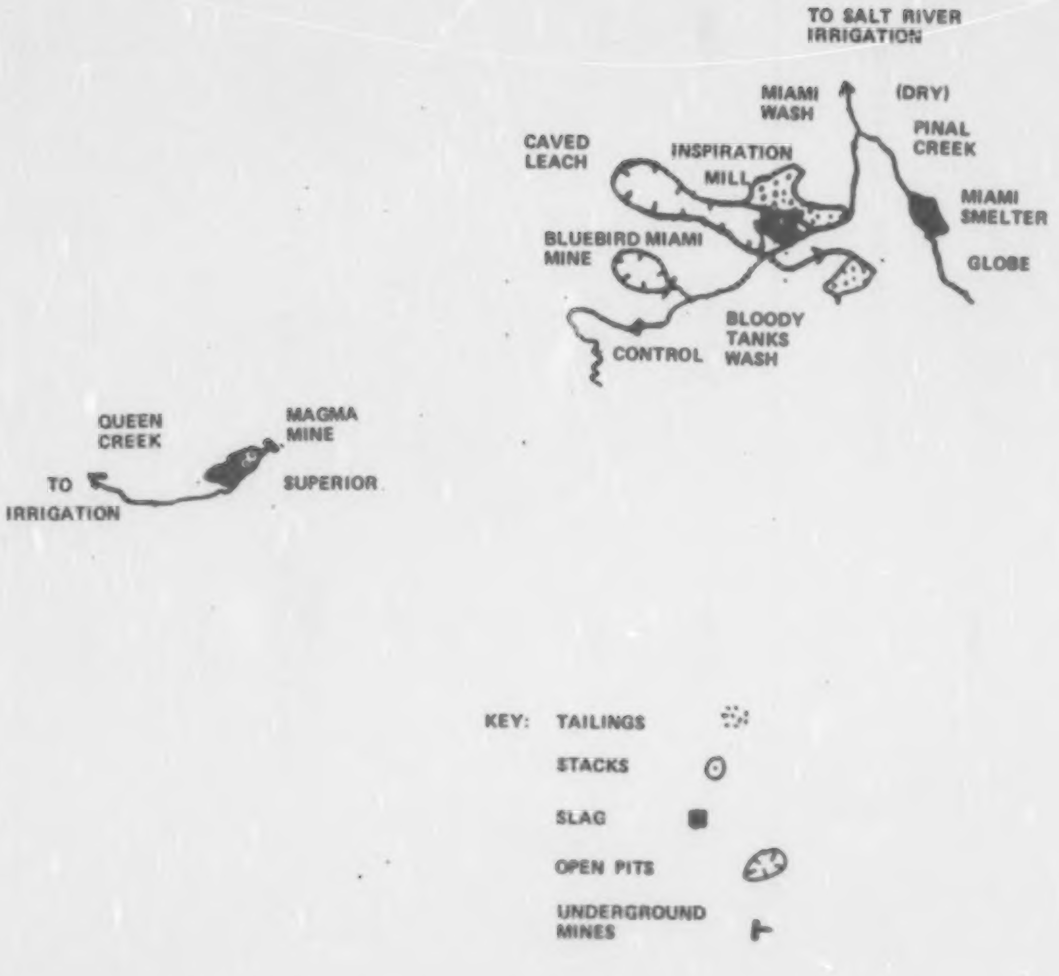

Figure 23 GLOBE-MIAMI AND SUPERIOR ARIZONA

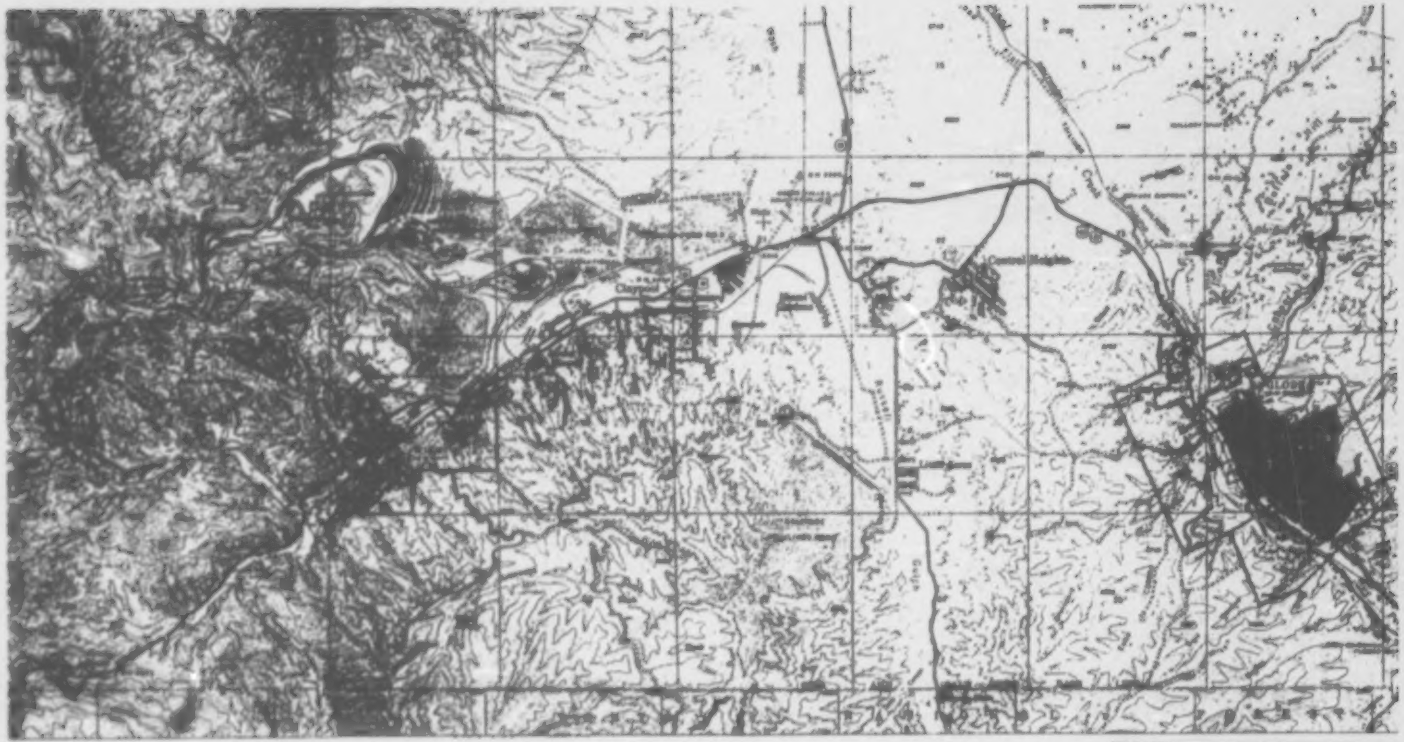

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Figure 24 TOPOGRAPHIC MAP OF THE GLOBE-MIAMI AREA

TABLE 35.

LEAD - ppm Inspiration Consolidated, Globe-Miami, Arizona

	water	sediment	phreatophyte roots
Bloody Tanks Wash upstream	<0.005	114	26
Bluebird mine runoff into wash	0.015	365	none
Inspiration			
concentrator	190 recycled	42000	18
smelter	"	5150	390
Miami Wash downstream	flood only	310	none

TABLE 36.

CADMIUM - ppm

Inspiration Consolidated, Miami, Arizona

	water	sediment	phreatophyte roots
Bluebird Mine	0.0015	<0.05	none
Concentrator	72 recycled	2.5	0.99
smelter	"	1.5	0.9
Miami Wash below Pinal Ck.	flood only	<0.05	none

Mammoth, Arizona

The large, low-grade San Manuel (Tiger) stock of Magma Copper Co. is mined on the pediment draining into the usually-dry San Pedro River (sampled) which joins the Gila at Hayden (Winkelman). The new Mammoth mill-smelter complex impounds tailings behind cyclone-separator dams as in Missouri. Water is recycled. Results of analyses for thallium, lead and cadmium are given in Tables 37, 38 and 39.

Morenci, Arizona

The Phelps-Dodge large open pit and mill-smelter complex, shown in Figures 25 and 26, recycles water from Chase Creek. The creek is dry below the complex. This creek drains into the San Francisco River which drains into the Gila below Clifton. A new company town has been built on the old tailings. Water from the river, wastes and mud from these operations and a ruined smelter site on the river were sampled. Results of these analyses are given in Tables 40-42.

Grant County, New Mexico

The east end of the porphyry district shown in Figure 27 produces significant zinc as well as copper and molybdenum. The Phelps-Dodge pit and mill at Tyrone in the Big Burro Mountains drained through dry washes (sampled, along with waste) into the Mimbres River. Water from the tailings is recycled.

In the Cobre Mountains, copper occurs around Laramide (50 million years old) porphyritic quartz monzonite stocks in a north-south trend which is followed by Whitewater Creek below the U. S. Smelting, Refining & Metals mine and mill at Fierro. Calspan sampled the recycled water and sediment, and the tailings runoff water and sediment at the headwaters of the creek. The creek ran down through Hanover past a closed mine and mill where we sampled biota, through Turnerville (mine waste and runoff sampled), and the ASARCO Groundhog mine (creek sampled below at Vanadium Post Office, no biota present).

TABLE 37.

THALLIUM - ppm

Magma Copper Co., Mammoth, Arizona

	water	sediment	slime
San Pedro River below mill & smelter	<0.003	<0.12	0.018

TABLE 38.

LEAD - ppm

Magma Copper Co., Mammoth, Arizona

	water	sediment	slime	algae	blackfly larvae
mill	recycled	2170	nothing alive		
smelter	"	3800	"	"	
San Pedro River	<0.01	50	7.5	20	>160

TABLE 39.

CADMIUM - ppm

Magma Copper Co., Mammoth, Arizona

	water	sediment	blackfly larvae
mill	recycled	0.44	nothing alive
smelter	"	0.24	" "
San Pedro River	<0.0005	0.5	>0.8

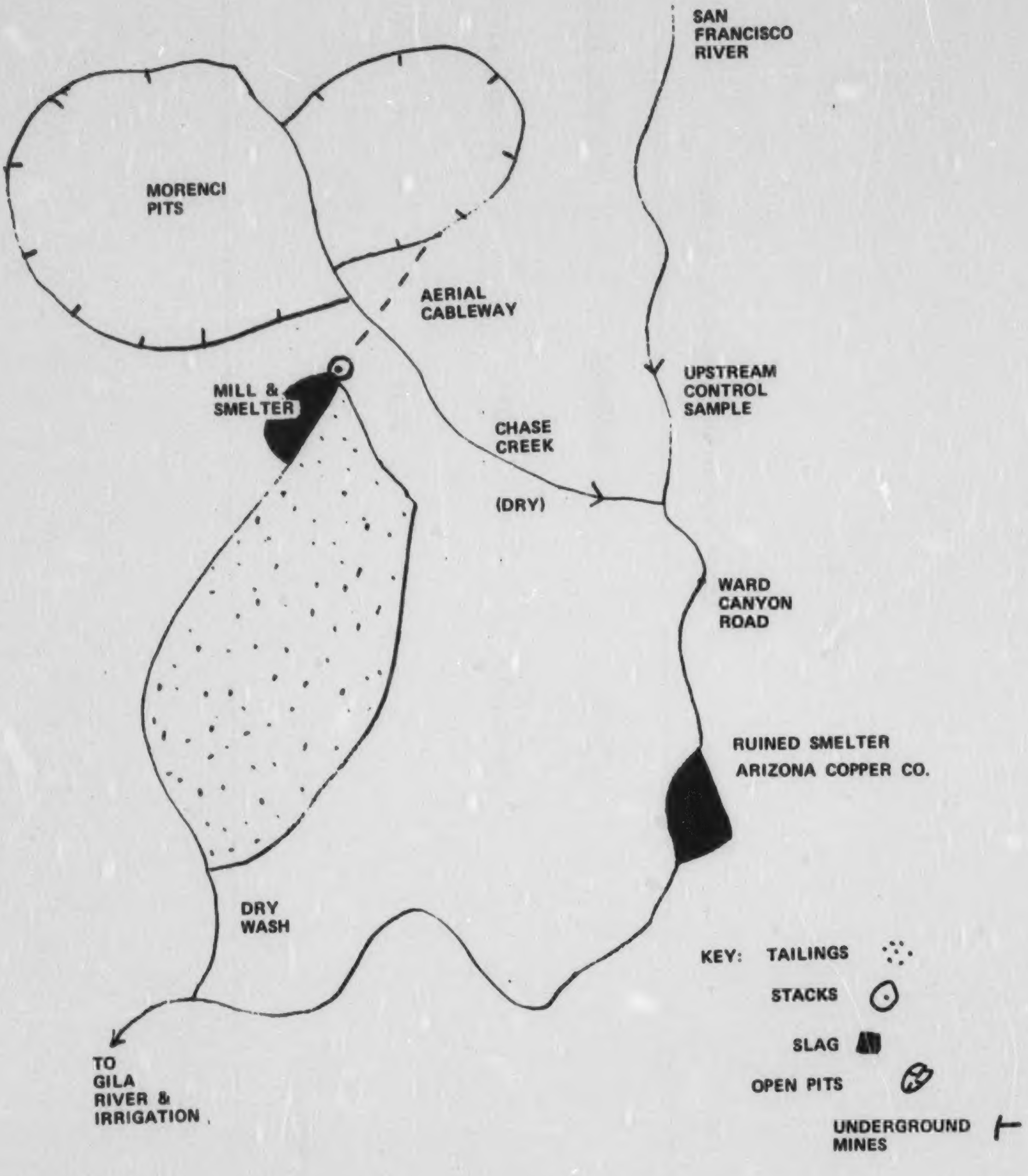

Figure 25 PHELPS DODGE MORENCI, ARIZONA

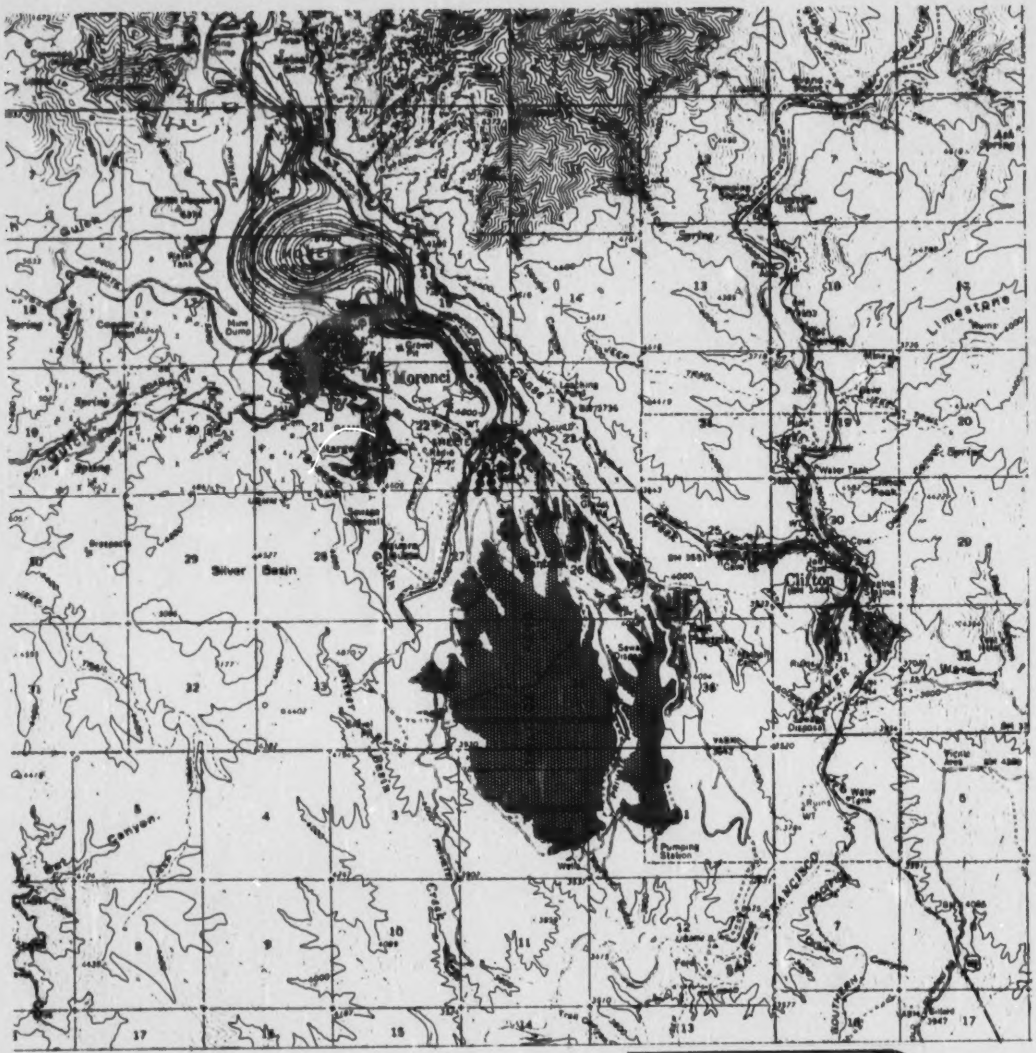

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Figure 26 TOPOGRAPHIC MAP OF THE MORENCI, ARIZONA AREA

TABLE 40.

LEAD - ppm

Phelps-Dodge, Morenci, Arizona

	sediment	blackfly larvae
San Francisco River above Clifton	32	--
Morenci pit	2860	none
mill	13300	"
smelter	1200-2200	"
Chase Creek below "	1530	"
Clifton smelter (ruined)		
(Arizona Copper Co.)		
floor	103000	none
slag	1090	"
San Francisco River downstream at		
Ward Canyon Road	73	28

TABLE 41.

THALLIUM - ppm

Phelps-Dodge, Morenci, Arizona

	sand
Clifton smelter (ruined) (Arizona Copper Co.) firebrick	0.13
San Francisco River at Ward Canyon Road	0.28

TABLE 42.

CADMIUM - ppm

Phelps-Dodge, Morenci, Arizona

	Sediment	Caddis larvae
Morenci pit	4.5	none
mill	4.9	"
smelter	0.63	"
Chase Creek	1.2	"
Clifton smelter (ruined)		
firebrick	270	"
slag	<0.05	"
San Francisco River	<0.03	2.5

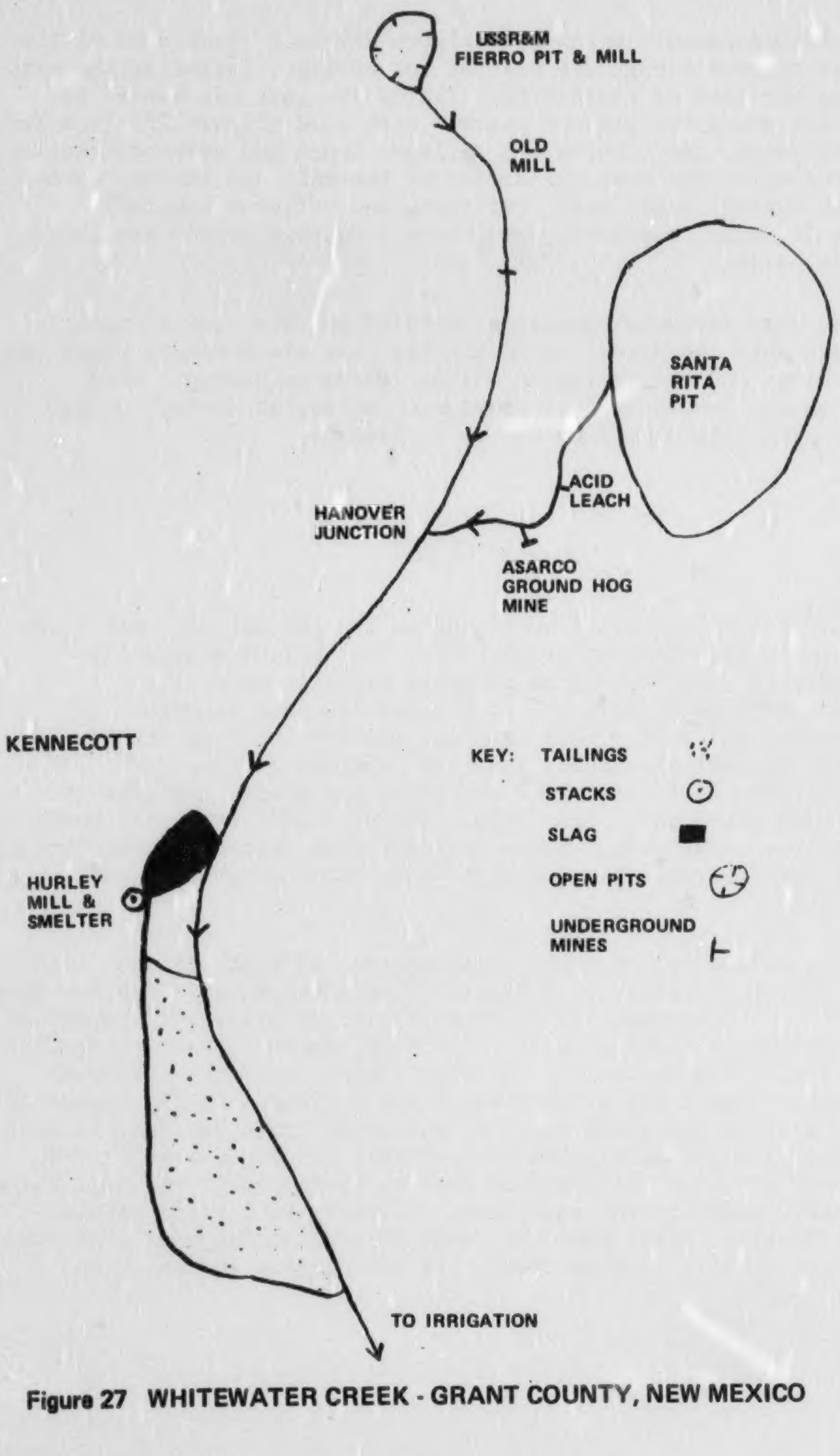

Figure 27 WHITEWATER CREEK - GRANT COUNTY, NEW MEXICO

The mile-wide Kennecott Chino pit (Figure 28) on a stock east of the trend has removed everything east of Turnerville, including the site of the former town of Santa Rita. 75% of the rock was hauled to waste piles above the pit and leached with acid (Figure 29) (sampled in the tributary creek below the railroad depot and above extraction and recycling). The rest was hauled to the mill and smelter downstream at Hurley (slag, soil, tailings, and effluent sampled). Analyses of water, sediments, and biota from this region are given in Tables 43-45.

Below the huge Kennecott mountain of tailings, Whitewater Creek disappears into the desert, although the peak flood waters reach the Mimbres River and the irrigated cotton fields at Deming. Acid fumes from the Kennecott acid plant and smelter at Hurley created serious vegetation damage as far up as Hanover.

El Paso, Texas

The ASARCO smelter is still operating on the Rio Grande. All river water used is recycled and evaporated. The smelter originally processed ores from the entire porphyry district as well as Chihauhua and Sonora, Mexico. At present old slag (sampled) is being crushed and sold. Soil samples, mud samples from the dry wash carrying smelter runoff, and river samples (water, muds, and biota) were collected above and below the plant. Results of analyses are given in Tables 46-48. The data indicated that toxic lead, thallium and cadmium fumes released from smelter stacks settled in soils and sediments but were not solubilized in water to any great extent.

In summary, the porphyry copper belt wastes had high measured lead concentrations, probably as a result of no present lead recovery from these ores. The largest source of pollution as previously reported was Mineral Creek (Tables 32-34, Figure 20) draining the Kennecott-Ray pit into the Gila River. The next largest operations were at the Kennecott-Santa Pit on Whitewater Creek (Tables 43-45, Figure 27). Although most of the flood flow of Whitewater Creek was used to irrigate cotton around Deming, New Mexico, some alfalfa was grown and fed to beef cattle. The low flow went to ground water recharge where ion exchange capacity was sufficient to remove most toxic metals. Some of the mine wastes found at Santa Rita had as high as 3.5% lead (but is essentially cadmium-free). It was eroding and leaching rapidly.

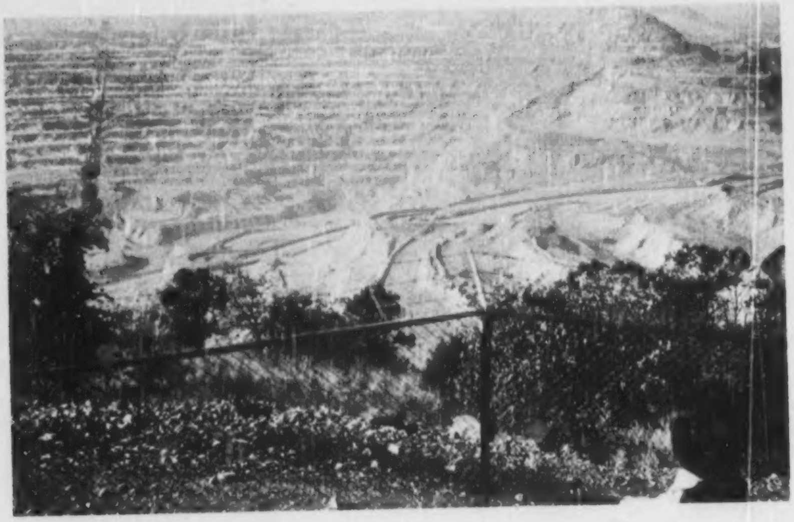

Figure 28 SANTA RITA - CHINO PIT

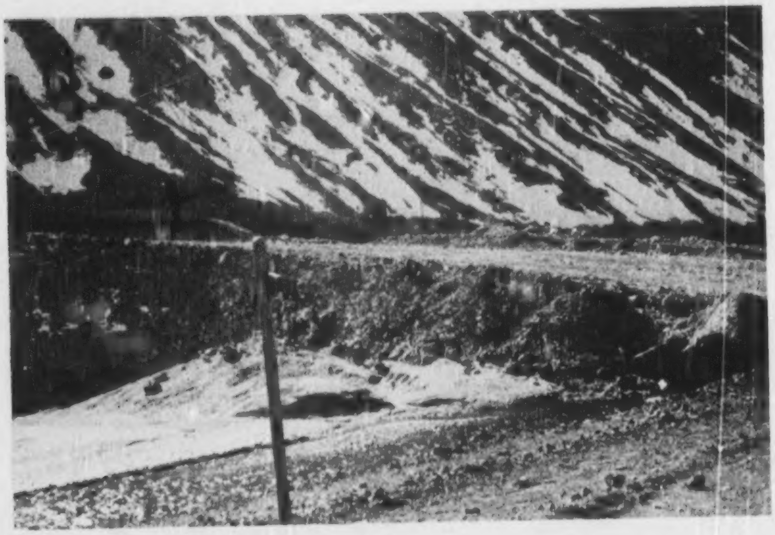

Figure 29 WASTE PILE AND ACID LEACH RUNOFF

TABLE 43.

THALLIUM - ppm

Whitewater Creek, New Mexico

	water	Sediment
U. S. Smelting & Refining at Fierro	<0.003 recycled	<0.08
old mill	<0.003	0.31
Kennecott		
Santa Rita pit	to leach	<0.08
acid leach	0.005 recycled	1.35
to irrigation at Hanover Junction	0.0037	<0.14
below Hurley mill	<0.003	0.082
smelter	recycled	0.19

TABLE 44.

CADMIUM - ppm

Whitewater Creek, New Mexico

	water	sediment	midge larvae
U. S. Smelting & Refining	0.0021 recycled	7.9 in soil facing Hurley smelter	none
old mill	0.0005	18-98	2.6
Kennecott			
Santa Rita pit	to leach	0.5	nothing alive
acid leach	0.16 recycled	4.3	" "
to irrigation	0.15	0.5	" "
below Hurley			
mill	0.0008	0.17	" "
smelter	recycled	1	" "

TABLE 45.

LEAD = ppm

Whitewater Creek, New Mexico

	water	sediment	midge larvae
U. S. Smelting & Refining at Fierro	0.02	1540	none
old mill	<.01	1100-3140	535
Kennecott			
Santa Rita pit	to leach	35000	nothing alive
acid leach	0.02 recycled	3500	" "
to irrigation at Hanover Junction	0.05	645	" "
below Hurley			
mill	0.01	216	" "
smelter	recycled	2190	" "

TABLE 46.

THALLIUM - ppm ASARCO, El Paso, Texas

	sediment
wash draining smelter	0.3
cemetery soil under stack	0.3

TABLE 47.

CADMIUM - ppm ASARCO, El Paso, Texas

	Water	Septic Sediment	Algae
Rio Grande upstream	0.0008	3	4.4
smelter	recycled	7.1	none
wash	flood only	19	none
cemetery soil	none	7.5	none
downstream	--	13	3

TABLE 48.

LEAD - ppm

ASARCO, El Paso, Texas

	water	sediment	algae
Rio Grande upstream	0.03	415	765
smelter	recycled	10200	none
wash	flood only	11600	none
cemetery soil	none	3140	"
downstream	--	1370	48

Magma Copper Co. operations at Mammoth (Tables 37-39) and Superior (Tables 29-31, Figure 23) are well dammed off from permanent surface streams although these, like all tailings dams, are subject to rainwash. Thalliferous slime in the San Pedro River was probably related to sewage treatment of domestic wastes from their town site.

The only thallium found in Globe-Miami (Tables 35-36, Figure 23) was 5 ppb in the acid leach water which was recycled through the mine wastes.

No cadmium was found at the control site upstream (less than 0.5 ppb in water and 50 ppb in sediment and biota). At Globe, the ruined Miami Copper Company (now Cities Service) smelter site had over 50 acres of old slag containing 98 ppb of thallium which was eroding into Pinal Creek.

No toxic metals were observed in the Phelps Dodge operations or on the San Francisco River below Clifton, Arizona (Tables 40-42, Figure 25), although flood erosion and leaching were a potential hazard. At Tyrone, New Mexico, a sample of their exposed mine wastes contained 73 ppb thallium, 43 ppm cadmium and 0.52% lead.

Planet Mine, Arizona

The Planet Mine, now closed, was sampled in January 1973. It produced the representative, high-temperature ores that are close to the active rhyolite volcanism and copper mineralization of the Salton Sea. The mine is on the Bill Williams River which drains into the Colorado above Parker, Arizona, (across from Earp, California). During operations from 1966 to 1970, a coarse, poorly-controlled acid leach was used to extract copper from the hematite-magnetite (Fe_2O_3-Fe_3O_4) ore sampled. Wastes sampled could be carried down the dry Planet Wash to the river during floods (Figure 30).

The highest concentration of thallium found in the Southwest, 5 ppm, was found at the closed Planet Mine (Tables 49-51). The Colorado River below the Bill Williams River and Planet Mine had the highest regional background with 21 ppb of thallium. It is an area of natural metal concentration.

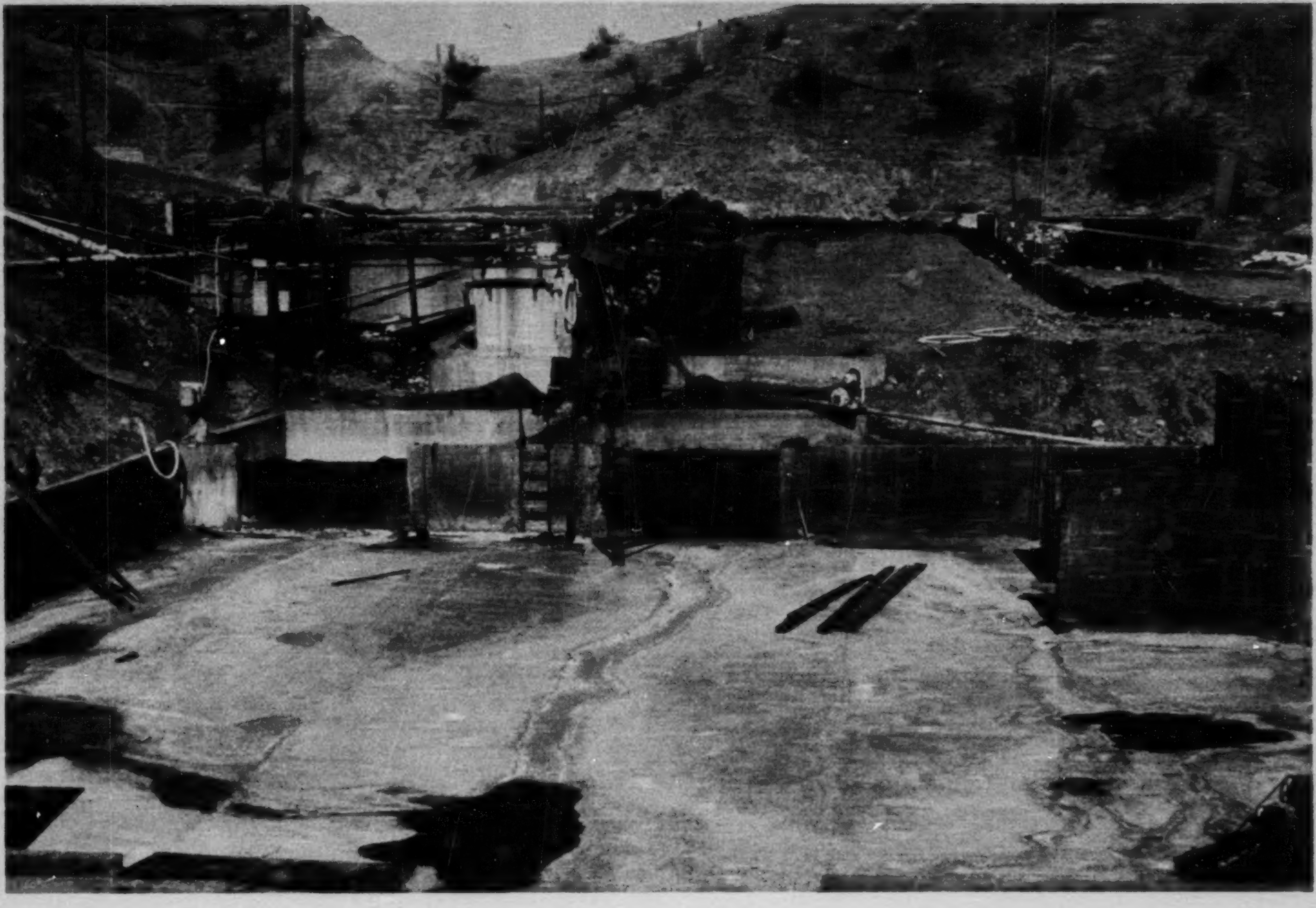

Figure 30 PLANET MINE ACID LEACH

TABLE 49.

THALLIUM - ppm   Powdered Metals Corp., Planet Mine, Arizona

	sediment	algae
acid leach (closed)	5.1	none
Bill Williams River at Planet Ranch below mine wash	<0.11	0.031
Colorado River at Parker below Bill Williams River	0.021	<0.07

TABLE 50.

CADMIUM - ppm

Powdered Metals Corp., Planet Mine, Arizona

	sediment	grass root	blackfly larvae	clam
acid leach (closed)	125	none	none	none
Bill Williams River	1	0.23	0.4	none
Colorado River	0.05	--	none	12

TABLE 51.

LEAD - ppm

Powdered Metals Corp., Planet Mine, Arizona

	water	sediment	algae	grass root	blackfly larvae	clams	fish
acid leach (closed)	dry	34200	none	none	none	none	none
Bill Williams River	0.01	37	16	35	42	none	9300
Colorado River	<0.01	32	110	--	none	170	--

Eastern Area

East St. Louis, Illinois

The American Zinc (now owned by AMAX) electrolytic refinery sampled in November 1972 is located in the floodplain of the Mississippi River. Spent acid and water were discharged into a serpentine lagoon discharging into a slough. This waste and two tank-bottom sludges (one being rich in Cu) dumped on its banks were sampled. The cupriferous waste was 12% zinc, 15% copper, 0.18% lead and 0.62% cadmium. The black sludge covering a large area west of the plant was 8.7% zinc, 0.75% copper, 0.45% lead and 0.1% cadmium. No thallium was detectable at the 90-280 ppb level.

Perth Amboy, New Jersey

A visit was made to Perth Amboy, New Jersey to examine plants typical of those situated on estuaries and tidal basins. It was found that the Asarco and Anaconda copper refining plants on the Raritan River estuary discharged into an area containing ten acres of waste. Next to Asarco along Arthur Kill, National Lead reclaims battery plates along with other operations, with over 25 acres of waste placed directly in the tidal marsh of the estuary. While none of its own operations may contribute Tl to the aquatic ecosystem, the dump was also used by surrounding industry and is believed to be a serious source of pollution, possibly including Tl. Waste material samples were obtained for the Asarco and Anaconda refineries. Samples were also taken at the Copper Pigments Chemical Works located at Sewaren, New Jersey.

Analyses of the collected samples were made using the Perkin Elmer Model 303 atomic absorption spectrometer. The results of these analyses are listed in Table 52. They are consistent with the amounts of thallium present in primary blister copper and the sludge-handling techniques of electrolytic refining. The Cottrell dusts which contained more hazardous concentrations, however, were only intermittently discharged to the aquatic environment.

The high thallium concentrations found in New Jersey were from small dumps of sludge and other highly toxic material which may not be representative. They were not resampled, however, because of the high level of background contamination throughout the entire industrial area including the Raritan River and Arthur Kill which drain these sites.

Table 52. THALLIUM ANALYSES FOR NEW JERSEY SAMPLES

Plant	Location	Sample	Thallium Concentration (ppm)
Anaconda Co.	Perth Amboy	Sludge Dump, near tailings pond	20
Anaconda Co.	Petth Amboy	Sludge Dump, fresh	21
Anaconda Co.	Perth Amboy	Sludge Dump, gley horizon	26
Copper Pigments Chemical	Sewaren	Sludge Dump	17

Palmerton, Pennsylvania

The old smelter and refinery complex of the New Jersey Zinc Co. is at Palmerton, Carbon County, Pennsylvania, on the Lehigh River just above the watergap through Blue Mountain where the river emerges from the Appalachian Mountains (Figure 31). Metal fumes from the low stacks at Hazard (West Palmerton) have killed almost all of the trees in the valley. Hot effluent (87°F, pH 4.5) from the smelter was sampled where it enters the Lehigh River along with slag and the resistant flora: algal slimes, mosses, and horsetails. Mud in the river bed contains 13% zinc, 590 ppm copper, 0.13% lead and 5.4 ppm cadmium. The river was heavily polluted by sewage from Lehighton, Jim Thorpe, and other communities above the smelter.

The acid plant and refinery in East Palmerton are on Aquashicola Creek which joins the Lehigh at the watergap. Cold effluent and sediment were sampled from the outfall at the creek where acid recovery appears to be satisfactory. The water contained only 90 ppb zinc. The sediment in the creek, however, contained 6.1% zinc, 0.7% copper, 290 ppm lead and 93 ppm cadmium.

Missouri Lead Belt

Tl is not significant in the extensive low-temperature lead-zinc ores of the mid-continent: Wisconsin, Illinois, Missouri, Kansas, Oklahoma, and Arkansas. Only those smelters in the midwest which have used significant amounts of Cordilleran or foreign ores and meet the other criteria were included in the study locations.

A field sampling program was conducted in the Missouri new lead belt or Viburnum trend an associated processing facilities.

The new lead belt runs over 30 miles north-south through the virtually uninhabited Ozark Plateau in Clark National Forest. A regional fracture trend in the Cambrian Bonneterre dolomite bedrock controls the occurrence of narrow caverns. These caverns extend 1200 feet below the surface down to the underlying insoluble pre-Cambrian granite basement which have been gradaully filled by reductive precipitation from circulating groundwater with up to 900 feet of sulfide ore. The sulfide ores are of massive galena

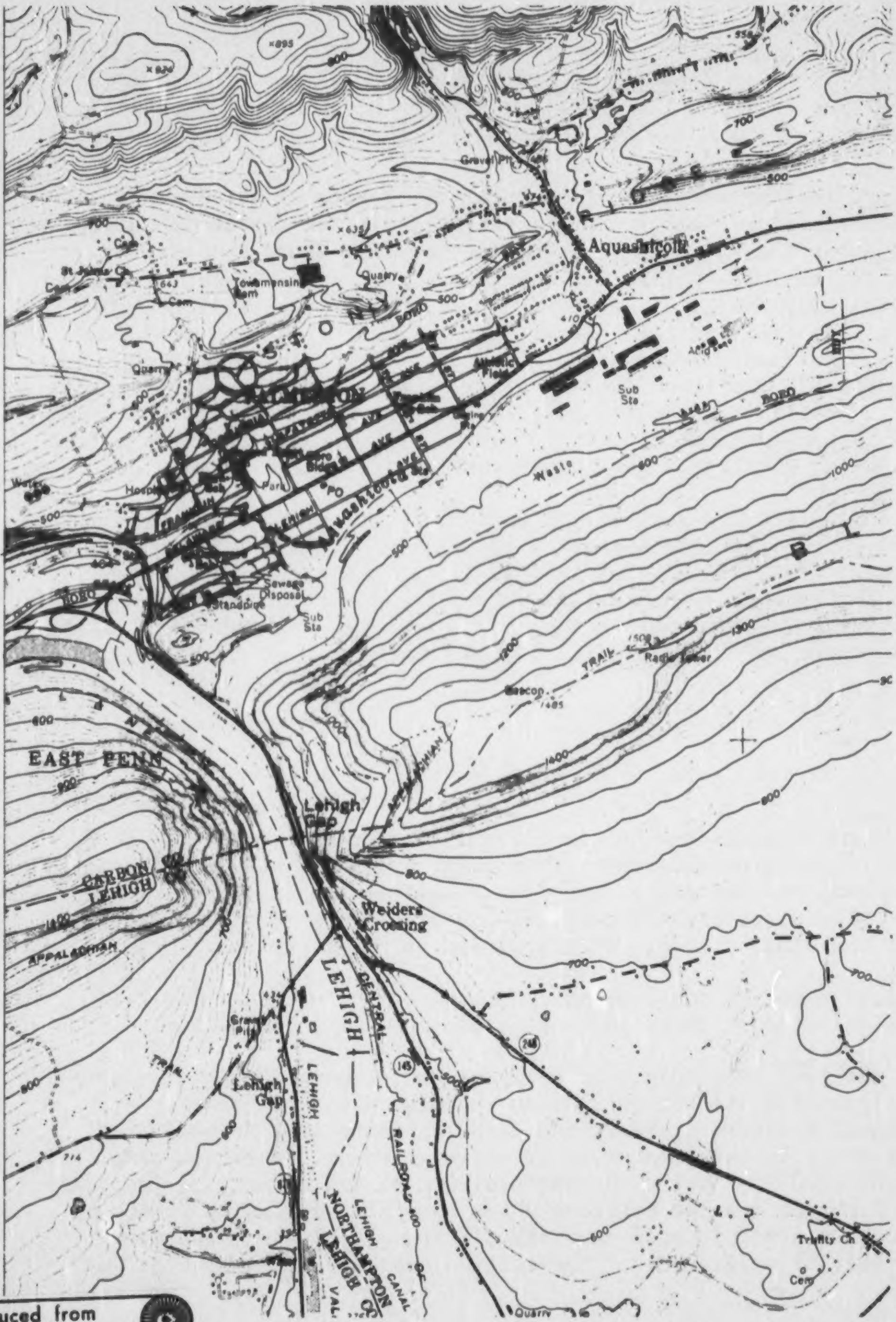

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Figure 30 TOPOGRAPHIC MAP OF PALMERTON, PENNSYLVANIA AREA

(PbS) with a thin rim of sphalerite (ZnS) and chalcopyrite ($CuFeS_2$) containing a small amount of AgS. The first mines at Viburnum, geophysically discovered, were opened in 1967 and the trend has become the largest lead-producing district in the world. The production required by the terms of Forest Service leases, coupled with recent restrictions on pigment and gasoline use, have cut the price of lead drastically.

A mine must pump 5,000 to 7,000 gallons/minute of groundwater to operate. Conventional operations run most of this relatively clear water through the mill and flotation concentrators to wash away waste rock flour. The high grade of the more massive galena ore often overloads the flotation system, and with the decline of lead prices, it is not economic to recover the last percent or more of the lead mined.

The muddy water, organic flotation agents, and wastes were discharged into any convenient nearby valley which could be provided by a series of dams made of the coarser mill tailings, by a cruder version of the cyclone separation process described for the White Pine facility. The final effluent thus varies with the pond size and mine water volume discharged.

The dark lead-bearing dolomite mud coated the stream bottoms with a gray algal-bacterial slime. The benthic fauna appeared to be intolerant of this lead-rich diet. The entire region is drained by various tributaries of the Mississippi River.

The air and water pollution by Pb, Zn, Cu and Mn are being studied on a continuing basis by B. G. Wixson and colleagues in Environmental Engineering at the University of Missouri-Rolla with support furnished by the National Science Foundation RANN Program.

St. Joe Operations

The most extensive producer in the area is the St. Joe Minerals Corp. This Corporation was the largest producer from the old lead belt 30 miles to the east. Conventional mines and mills were in operation at Viburnum and Fletcher, and under construction at Brushy Creek. Their ponds were minimal in size, the dams were eroding rapidly, and the effluent from their plants was virtually abiotic, apparently due to excess organic flotation agents discharged. The milled ore was shipped to the old company smelter on the Mississippi at Herculaneum. All of their active facilities were sampled.

The most serious waste problem is the effluent from the Fletcher mill close to Bee Fork. The settling ponds are narrow and already full of tailings, except for the small, shallow lagoons in the floodplain. The virtually abiotic effluent into Bee Fork was sampled along with the upstream control biota. The effluent was sampled where mixing first occurs (Figure 32) and two miles further downstream. The effluent contained 0.12 ± 0.003 ppm of lead by atomic absorption analysis. Recent severe local flooding had reduced the benthos all along the Fork, which receives flash runoff from a cleared area upstream around the small town of Bunker. Aanalyses of lead and cadmium in water, sediments and biota are given in Tables 53 and 54.

Two mines at Viburnum were in operation along Indian Creek, a tributary of the Meramec River. The ore from the downstream mine was trucked up to the mill at the upstream mine. The truck route, paralleled by a large-diameter pipe which conveyed the mine water to the upper pond, was built along the creek. Samples were taken from the relatively clear uppermost pond (which has a thick mat of the algae Chara), from mill tailings discharge, and from the creek below the lowermost dam which contained mill wastes. Analyses of lead and cadmium in water, mud and biota are given in Tables 55 and 56.

In summary, the lead levels in waters from the new Missouri lead belts were high, as shown in Tables 53 and 55. The low levels of lead discharge which can be achieved were shown below the Ozark Lead Co. mine and mill which recirculates its water through tailings ponds. In the final effluents, lead was below 10 ppb, zinc below 100 ppb and cadmium below 1 ppb. Only copper (44 ppb) was above the levels in uncontaminated control streams. Cadmium values were all low.

MOLOC Complex, Missouri

The largest facilities center around the Homestake-American Metals Climax (Missouri Lead Operating Co.) smelter south of Bixby. Its slag is presently being stockpiled although it was used on roads until recently. The effluent is combined with

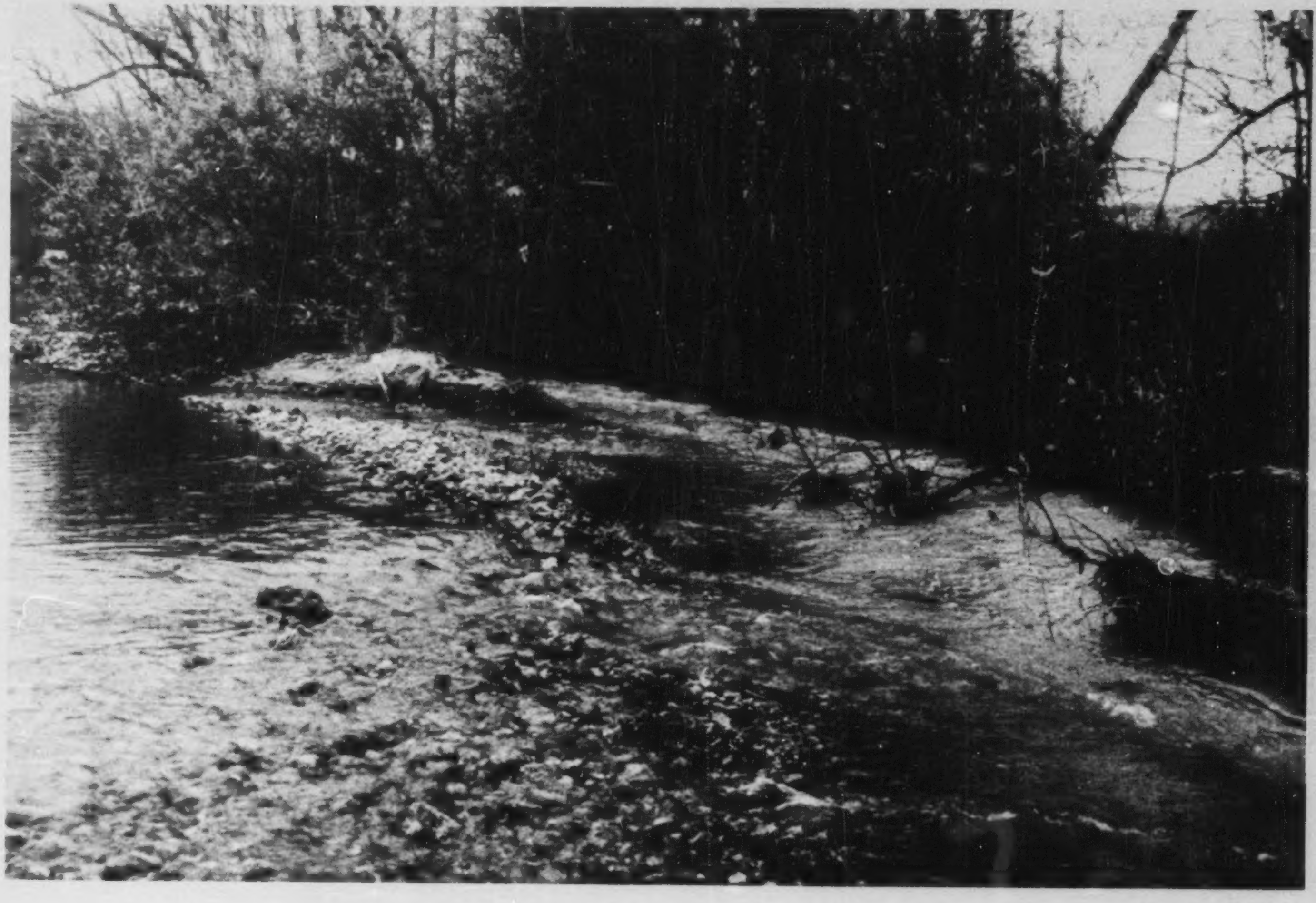

Figure 32 TAILINGS EFFLUENT AT BEE FORK CREEK

TABLE 53.

ST. JOE FLETCHER MINE, MISSOURI

LEAD -- ppm

	Water	Sediment	Algae	Caddis Larvae	Crayfish	Minnows
Bee Fork above outfall (below highways, lily farm and Bunker, Mo.)	∠0.01	350	(Myriophyllum) none	11	10	32
Mill tailings pond	0.12-0.13	---	112	71	none	none
Bee Fork below outfall	0.003	38	19	97	19	3.9

TABLE 54.

ST. JOE FLETCHER MINE, MISSOURI

CADMIUM -- ppm

	Water	Sediment	Algae	Caddis Larvae	Crayfish	Minnows
Bee Fork above	0.001	0.5	none	2.2	0.17	0.25
mill tailings pond	0.001-0.002	---	0.28	2.6	none	none
below	0.001	1	0.1	1.8	0.22	0.08

TABLE 55.

NEW LEAD BELT, MISSOURI

(VIBURNUM)

LEAD - ppm

	Water	Mud	Algae (Chara)	Minnows
Mill	pumped from mine	1250	none	---
Pond 1	4.3	500	63	---
Pond 2	0.55	---	none	---
into Indian Ck.	0.04-0.09	300	none	2

TABLE 56.

NEW LEAD BELT, MISSOURI
(VIBURNUM)
CADMIUM -- ppm

	Water	Mud	Algae (*Chara*)
Mill	pumped from mine	2.5	none
Pond 1	0.008	<1.3	3
Pond 2	0.001	2.5	none
into Indian Ck.	0.001-0.002	----	none

tailings from their Buick mill and the adjacent Magmont mill of Cominco-American (Kennecott Copper and partners), settled, recirculated, and discharged into Strother Creek. The large volume of mine water from this huge operation fills Strother Creek over capacity. Much larger pond capacity would be required to allow evaporation of this flow. Separation of the tailings, however, and recirculation of the mill water required could be achieved.

Samples were taken of slag and tailings at the complex. Effluent, sediment and biota samples were taken below the final serpentine spillway (designed by Wixson to promote algal growth) above Asher Cemetery. Results of chemical analyses are given in Tables 57 and 58. The analysis showed 0.27 ± 0.03 ppm Pb in this water. Wixson found up to 0.83 ppm Pb in the water at this point and approximately 60 ppm Pb, 7-14 ppm Zn, 0.25-0.7 ppm Cd, and 3-7 ppm Cu in Strother Creek mud. Control samples were taken along Neals Creek, which joins Strother Creek below the last MOLOC dam.

Significant Tl was not found in ASARCO or MOLOC discharges, effluent or river samples. Tl levels determined by plant laboratory personnel from emission spectroscopy were clearly below 1 ppm in any waste stream. Serious Pb pollution was admitted due to the slag-granulating cooling water which must be recirculated to meet current effluent standards.

Ozark Lead, Missouri

This mine and mill in the most isolated location have the most nearly complete recirculation system yet in the trend. A small, nearly abiotic effluent discharged into Sweetwater Creek was sampled· 1 ppb Cd and 44 ppb Cu were found.

Glover, Missouri

The ASARCO Custom smelter on Big Creek has been recently rebuilt. It serves Ozark Lead and some of the remaining minor production from the old lead belt. Water is recirculated at this smelter. The slag effluent and sediment were sampled by Calspan, and water from Big Creek was sampled above and below the small effluent discharge which contained 53 ppb Cd, 220 ppb Pb, 2.2 ppm Zn and 3 ppb Tl.

TABLE 57.

MOLOC Complex, MISSOURI

Lead - ppm

	Water	Sediment	Algae	Larvae (Caddis)	Crayfish	Minnows
Clean control streams	$\leq$ 0.013	50	20	44	5.7	2.9-8.4
Magmont mill	5	1550	none	none	none	none
Smelter	none	10500	none	none	none	none
Strother Creek	0.27	850-2050	none	blackfly 320	48	5.6

TABLE 58.

MOLOC Complex, MISSOURI

CADMIUM -- ppm

	Water	Sediment	Algae	Larvae (Caddis)	Crayfish
Clean streams	≤ 0.002	0.5	0.14	1.7	0.29
Magmont Mill	0.002	13	none	none	none
Smelter	none	8.2	none	none	none
Strother Ck.	0.001	0.5-1.3	0.13-0.21	3.4	2.5

St. Francois Old Lead Belt

St. Joe Minerals Corp. has extensive facilities in the old lead belt on the Bonneterre outcrop in the St. Francois Mountains where lead has been know to exist since the 18th century.

A mountain of coarse gravel-sized tailings, over 300 feet high, with visible galena in Flat River was sampled. The closed Federal mine and mill on Shaw Creek was surrounded by extensive waste piles and tailings ponds. The creek was sampled at its mouth. Analyses of water, slag, sediment and biota for lead and cadmium are given in Tables 59 and 60.

Herculaneum

The St. Joe smelter was built in 1864 on a narrow terrace between high cliffs and the Mississippi River. Its capacity is being increased by high-rise construction. The hot effluent, including sanitary sewage and acid-plant leakage was discharged directly into the main deepwater channel of the river from a new tall structure. A water recirculating system has been "under construction" for years. The slag and river above the smelter were sampled, but access to the present effluent could not be obtained. The St. Joseph Mineral Company's slag piled along the bank of the Mississippi River at Herculaneum contains from 1 to 3.3% lead, 1 to 9.2% zinc, 300 to 3800 ppm copper and 14 to 250 ppm cadmium. The most toxic of this material was being bulldozed into the river in large quantities in the process of building a sanitary sewage treatment plant next to the smelter.

White Pine Mine and Smelter, Michigan

The Copper Range, White Pine mine and smelter, with a large tailings area, is on the Mineral River draining into Lake Superior, cleanest and coldest of the Great Lakes. These waters still support commercial fisheries and provide the public supply for tens of millions of people. The wastes and waters from the smelter and mill were sampled down to the lake on August 24-26, 1972.

In the copper processing at White Pine, pit-run shale is milled to a mud and most of the CuS concentrate floated off with surfactants. The fine tailings from the mill are neutralized with lime and piped

TABLE 59.

OLD LEAD BELT, MISSOURI -- ST. FRANCOIS

LEAD - ppm

	Water	Slag	Sediment	Algae	Caddis Larvae
300 ft. high pile north of Flat River	none	none	12000	none	none
St.Joe Federal mill	closed	none	1500	none	none
draining into Shaw Ck. at Flat River	0.23	none	6500	2800	2200
ASARCO Glover smelter	0.22	9500	25	2230	none
draining into Big Creek	0.013	none	---	---	---

TABLE 60.

OLD LEAD BELT, MISSOURI -- ST. FRANCOIS

CADMIUM -- ppm

	Water	Slag	Sediment	Algae	Caddis Larvae
high pile	none	none	1.3	none	none
St. Joe Federal mill	closed	none	7.5	none	none
draining into Shaw Creek	0.001	none	1.3	0.96	2.1
ASARCO smelter draining into	0.053	12	300	1330	none
Big Creek	<0.001	none	---	---	---

to storage behind earthen dams. The storage area is gradually covering the large region between the mine and Lake Superior. Some of the coarser tailings are used to build the dam and fill the mine. Mill water, rain and snowmelt are decanted with minimal mud (restricted by state standards) and collected in Native Creek (Figure 33), a deep stream 3 to 6 feet wide, which joins the Mineral River where it is 50 feet wide and one foot deep just above Lake Superior.

The wet concentrate from the mill is melted in reverberatory furnaces. Up until now, pyrites have been added to enhance sulfur concentration and reduce smelting costs. These pyrites have been acquired from Bethlehem Steel's Cornwall, Pennsylvania mine which also supplies the Sparrows Point, Maryland acid plant. Because the pyrite deposits are nearly exhausted and in an effort to reduce sulfur emissions from the stack, the concentration of pyrites used in the White Pine processing is currently being minimized and presumably will be eliminated.

For this reason, the nature of the slag and the water effluents is now in a state of transition. In any case, slag from the furnaces is dumped, crushed, washed and as much as possible sold for road and other use. Wash water and other smelter runoff settles in a small new pond and flows through the woods and Bannister Creek, 3 to 5 feet wide, into the Mineral River (Figure 34), where it is 12 feet wide and 3 feet deep, just below the Carp Lake Township Dump.

Our survey of the Mineral River (Figures 35 and 36) started above the smelter and company town where it is 1 to 2 feet wide with a complete normal boreal biota consisting of algae, aquatic moss, caddisfly larvae, water striders and minnows. The river was then followed past the facilities, including a sewage treatment plant and uncontrolled erosion from the slag pile, down to the junctions with the muddy influents.

With the assistance of plant environmental-control personnel, we sampled soil, tailings, pond waters and effluent into both Native and Bannister Creek. Results of these analyses are given in Tables 61-64. The mud in the Mineral River below Bannister Creek continues out into Lake Superior to such an extent as to reduce the biota to a few algae and water striders. The latter probably feed primarily on terrestrial insects which fall in from the forest.

No thallium was detected, even in recycled flue dusts. Significant levels of lead, copper and zinc are present.

Other Known Thalliferous Sulfide Accumulations

The high-capacity plant in the Salt Lake City, Utah area (Garfield and Tooele) drains directly into Great Salt Lake, which is essentially a lifeless, saturated brine.

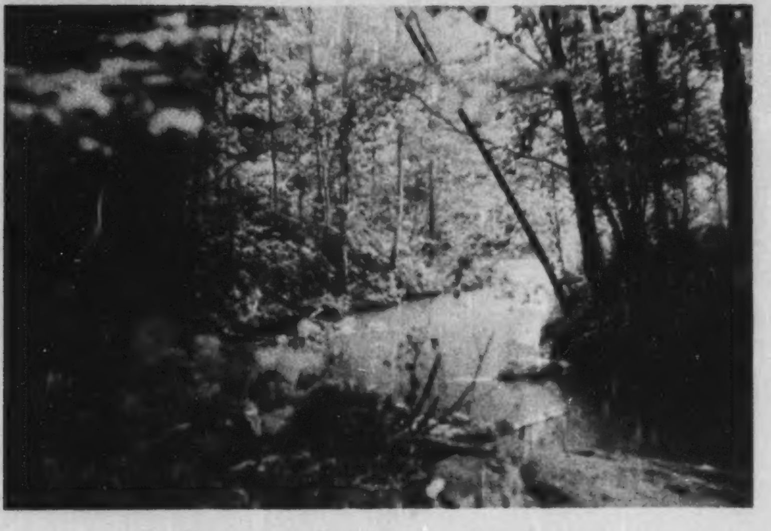

Figure 33 NATIVE CREEK (WHITE PINE)

Figure 34 BANNISTER CREEK FLOWING INTO THE MINERAL RIVER SHOWING TURBIDITY

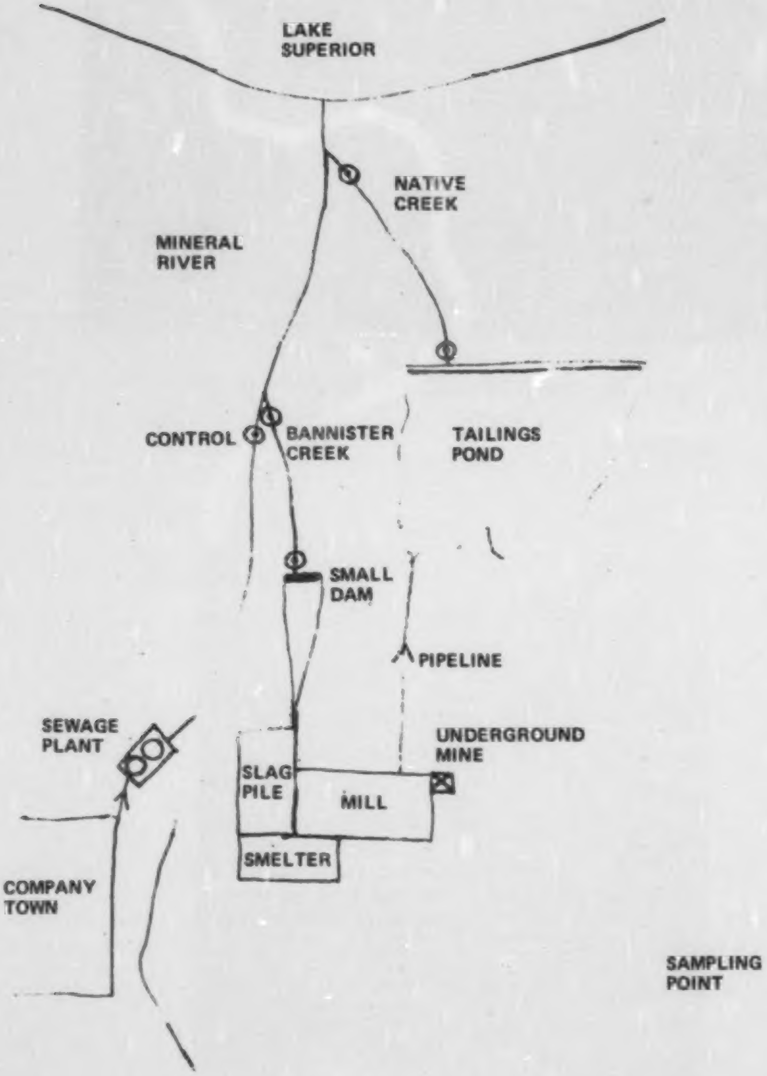

Figure 35 WHITE PINE, MICHIGAN

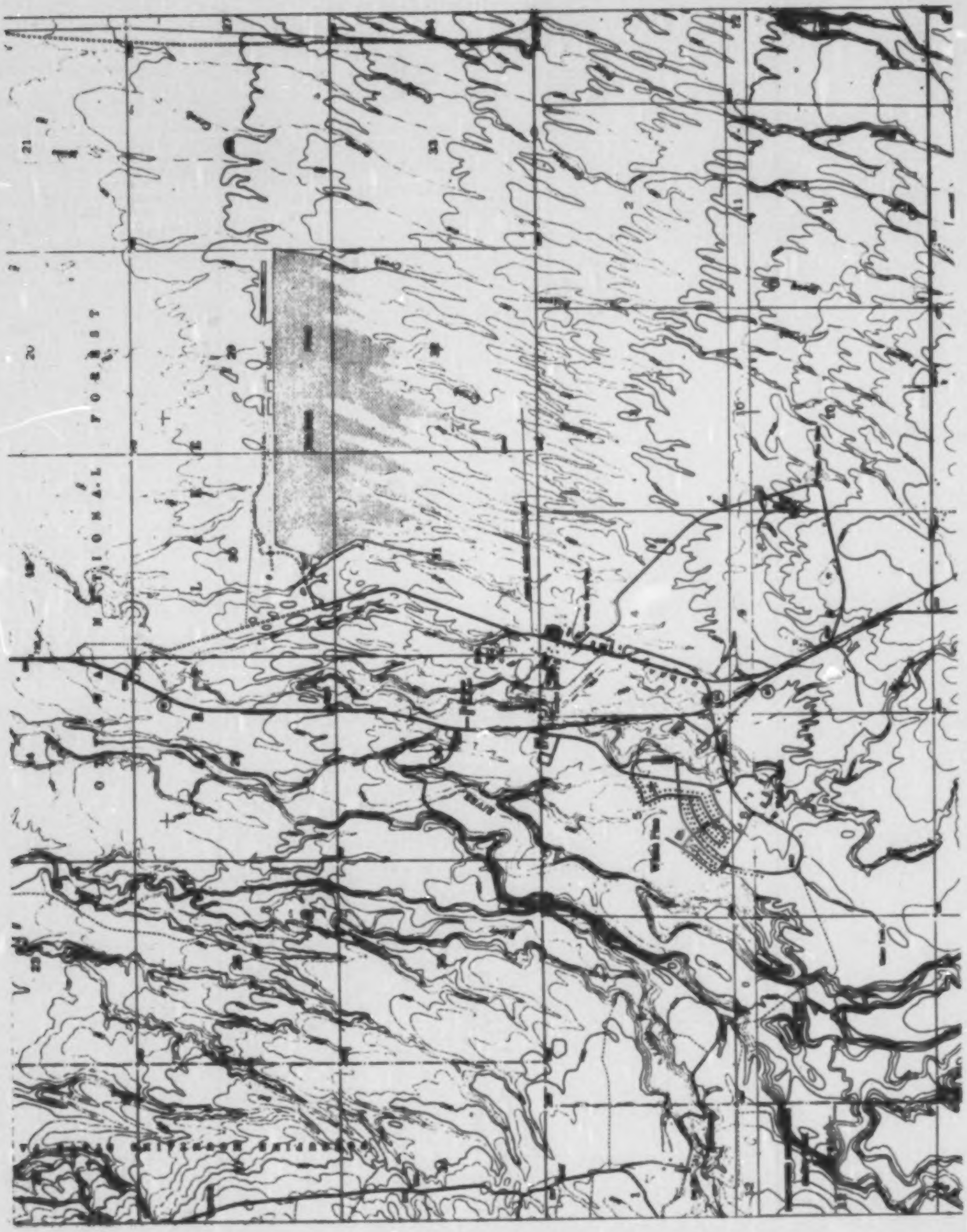

Figure 36 TOPOGRAPHIC MAP OF THE WHITE PINE, MICHIGAN AREA

Reproduced from best available copy.

TABLE 61.

WHITE PINE, MICHIGAN

LEAD -- ppm

		Sediment	Algae	Larvae (Caddis)	Fish (stickleback)
Control (Mineral River below sewage plant)		1.1	45	--	36
Mill tailings	at outfall	0.29	128	--	73
(Native Creek)	at junction	0.08	24	190	none
Slag runoff	at outfall	0.33	none	none	"
(Bannister Creek)	at junction	0.13	"	"	"

TABLE 62.
WHITE PINE, MICHIGAN
CADMIUM - ppm

	Sediment	Algae	Larvae	Fish
Control	0.057	0.72	--	1.0
Tailings at outfall	0.14	3.5	--	11
junction	0.008	0.88	11	none
Slag runoff at outfall	0.12	none	none	"
junction	0.011	"	"	"

TABLE 63.
WHITE PINE, MICHIGAN

COPPER - ppm

	Sediment	Algae	Larvae	Fish
Control	240	360	--	55
Tailings at outfall	4600	5000	--	360
junction	1400	52	230	none
Slag runoff at outfall	1300	none	none	"
junction	1300	"	"	"

TABLE 64.

WHITE PINE, MICHIGAN

ZINC - ppm

	Sediment	Algae	Larvae	Fish
Control	22	81	--	55
Tailings at outfall	not analyzed	1300	--	190
junction	13	--	300	none
Slag runoff at outfall	180	none	none	"
junction	67	"	"	"

The known Tl reserves in the dump at Mercury, Utah (Sargent, 1952) were not near any permanent water and drain through ephermeral channels into dry Rush Lake. Inactive and secondary plants are not included in the present list, although the locations of a number of such waste concentrations are known.

The smelter at Matthiessen and Hegeler Zinc Company (Meadowbrook), Spelter, West Virginia, below Clarksburg, has apparently filled an entire bend in the river up to 20 feet, over 1/2 mile long, of what was floodplain. High rainfall of the region tends to promote leaching. The river, like most of those in the Coal Measures, is entrenched without a wide floodplain so that catastrophically high water levels may occur. However, the river is too polluted to provide much data on bioconcentration.

Lithopone production has become negligible. A small amount has recently been exported to South Vietnam. Lead-free ZnO has replaced it domestically. The largest plant, American Zinc Company's plant at Columbus, Ohio (which also produces sulfuric acid) is not situated on a surface stream. Any surface runoff apparently runs into a nearby cemetery and percolates into the soil.

Steel Mills

Blast furnaces formerly using anthracite coke at the main Bethlehem Steel Co. plant are closed. Current metallurgical operations use electrical furnaces to produce high grade specialty steels. The slag dump and Lehigh River water at this plant were sampled. Analysis of these and other steel slags previously sampled indicates that ferrous metallurgy produces little serious heavy-metal hazard. No thallium was detected. The gross observable biological effects are negligible compared with copper, lead and zinc operations.

Sulfuric Acid Plants - Copper Basin, Tennessee

Up to 3 1/2% Tl has been reported in sulfuric acid made from thalliferous pyrites (Guelin, 1938). Sulfuric acid made from pyrite (FeS_2) may concentrate Tl in the exit stack gas. The original Cottrell precipitator was installed to remove sulfuric acid mist at the American & Selby, California copper smelter in 1909. A decision was made to sample from the Copperhill smelter and acid plant within the large Copper Basin region of Tennessee.

The Copper Basin (Figures 37 and 3[illegible]) is an eroding devegetated wasteland six miles across centered near Ducktown, Polk County, and covering the southeast corner of Tennessee. Chalcopyrite, pyrite, and other sulfides similar to the rocks mined at Kellogg and White Pine are found in black schists of the Ocoee series. Mines are scattered throughout the basin with an active mill and abandoned smelter at Isabella (Ducktown) on Potato Creek and an active smelter with a large acid and chemical plant at Copperhill on the Ocoee River.

The control sampling stations for this region were the headwaters of the Burra-Burra Creek above the tailings pond (see Figure 37) and the Ocoee River at the Tennessee-Georgia border. A number of areas suspected of heavy metal concentration were sampled. These included ore from an abandoned mine pit near the tailings pond, the tailings pond itself, drainage from the tailings pond into Potato Creek, the Copperhill smelter wasteweir on Davis Mill Creek and a ditch (West Newton) draining through the vicinity of the smelter to the Ocoee River. The Ocoee River was further sampled below the Rogers Bridge and 8 miles downstream at the #3 powerhouse. Results of analyses are given in Tables 65-69.

The tailings pond was found to contain 1.4 ppm phenol, apparently from chemical wastes in the mill water. Relatively large amounts of thallium are stored in the tailings pond as a byproduct of pyrite mining and sulfuric acid production. The tailings pond is subject to flood overflow. Cd could not be detected anywhere in the Ocoee River water or uncontaminated control stream waters but was found in all the outfalls and creeks leading from the mill and smelter. Copper, zinc, lead and cadmium showed tendency to accumulate in aquatic roots and mosses but not in algae and fish This probably results from direct exchange between sediments and root hairs.

Ore from an abandoned mine pit near the tailings pond contained 11% copper along with 900 ppm zinc, 300 ppm lead and 1.8 ppm cadmium. The slags at Isabella and Copperhill vary from 500 to 1400 ppm copper, 350 to 4800 ppm zinc, 75 to 200 ppm lead and 1/2 to 1 ppm cadmium. Thallium was not detectable at the 100 ppb level in any of these samples. Thallium was not detected (at a sensitivity of 1 ppb) in any water or biota samples collected from this region.

Fuel Burning Plants

Some coal deposits, notably anthracite of high temperature diagnetic origin, contain considerable amounts of thallium associated with

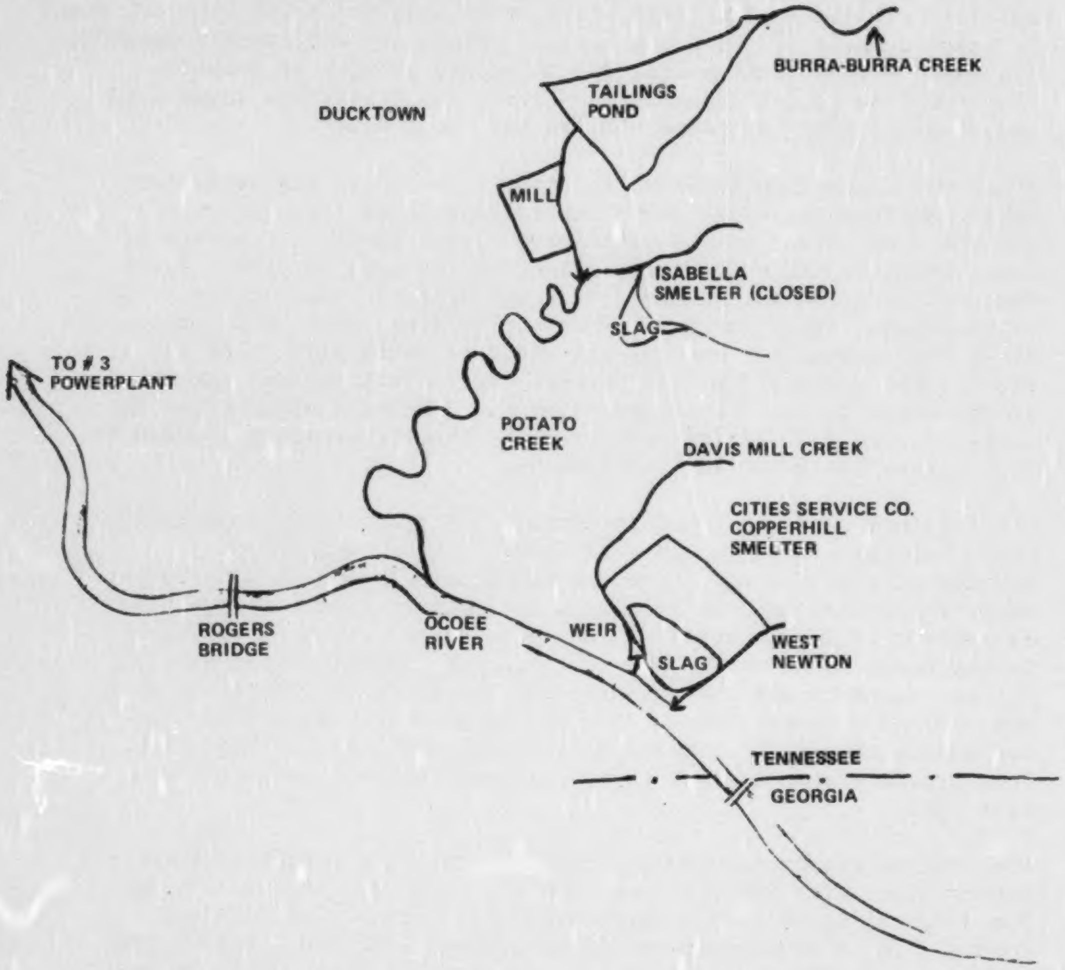

Figure 37 MAP OF COPPER BASIN, TENNESSEE

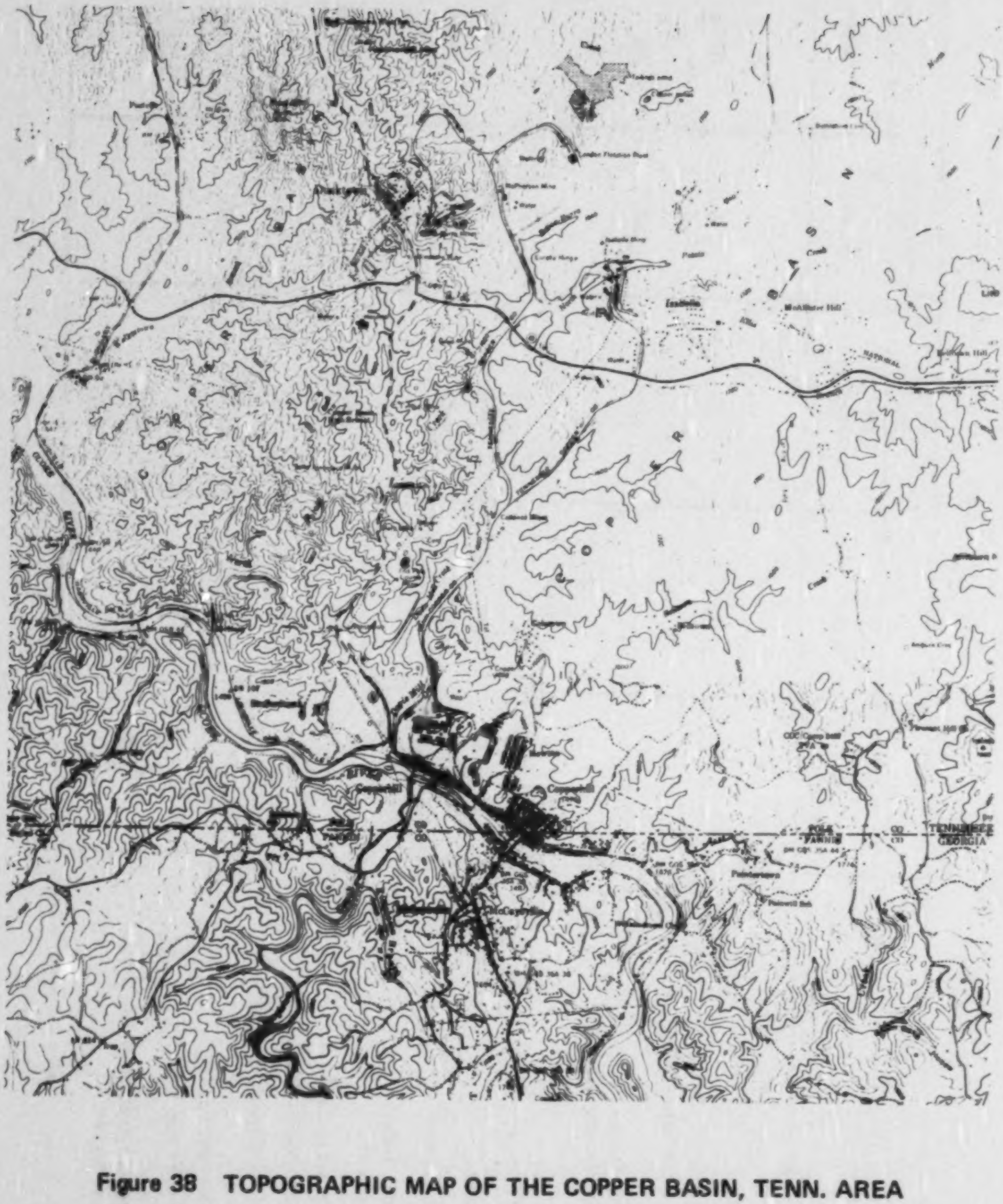

Figure 38 TOPOGRAPHIC MAP OF THE COPPER BASIN, TENN. AREA

TABLE 65.

COPPER BASIN, TENNESSEE

ZINC -- ppm

		CONCENTRATION				
	pH	Water	Sediment	Aquatic Roots	Algae	Minnow
Controls:						
headwaters of Burra-Burra Ck. at Jarnigan Mtn.	4.4	0.15	25	8.6	none	none
upstream Ocoee River at Georgia state line	5.0	0.1	550	540	50	35
Contaminated:						
mine waste	none	none	900	none	none	none
tailings pond		0.15	10000	15	none	none
draining into Potato Creek	3.5	1.5		none	none	none
smelter waste weir on Davis Mill Ck.	3.9	9.8	900	none	none	none
W. Newton ditch (at gate)	3.9	4.5	120	none	none	none
Ocoee River below Rogers Bridge	4.7	0.8	8800	450	none	none
8 miles downstream at #3 powerhouse	4.5	0.25	1500	41	aquatic moss 224	none

TABLE 66.

COPPER BASIN, TENNESSEE

COPPER -- ppm

	CONCENTRATION			
	Water	Sediment	Aquatic Roots	Algae
Controls:				
headwaters	$<$ 0.01	40	5	none
upstream Ocoee R.	$<$ 0.01	30	430	75
Contaminated:				
mine waste	none	2100	none	none
tailings pond	0.01	2100	4.2	none
into Potato Ck.	0.28	--	none	none
smelter weir on Davis Mill Ck.	4.2	900	none	none
W. Newton ditch	0.31	280	none	none
Ocoee R. below creeks	0.52	3800	450	none
8 miles downstream	0.06	500	25	Aquatic Moss 240

TABLE 67.

COPPER BASIN, TENNESSEE

LEAD -- ppm

	CONCENTRATION			
	Water	Sediment	Aquatic Roots	Algae
Controls:				
headwaters	< 0.05	< 12	< 5	none
upstream Ocoee R.	< 0.05	75	< 110	25
Contaminated:				
mine waste	none	200	none	none
tailings pond	< 0.05	250	4.2	none
into Potato Ck.	0.3	---	none	none
smelter weir on Davis Mill Ck.	1.0	170	none	none
W. Newton ditch	0.1	150	none	none
Ocoee R. below creeks	0.2	2550	245	none
8 miles downstream	< 0.05	150	< 1.6	Aquatic Moss 60

TABLE 68.
COPPER BASIN, TENNESSEE
CADMIUM -- ppm

	CONCENTRATION				
	Water	Sediment	Aquatic Roots	Algae	Minnow
Controls:					
headwaters	< 0.003	0.1	0.25	none	none
upstream Ocoee R.	< 0.003	0.4	6.4	0.4	0.5
Contaminated:					
mine waste	none	1	none	none	none
tailings pond	0.007	7.5	0.15	none	none
into Potato Ck.	0.003	---	none	none	none
smelter weir on Davis Mill Ck.	0.002	2	none	none	none
W. Newton ditch	0.006	10	none	none	none
Ocoee R. below creeks	< 0.003	10	1.9	none	none
8 miles downstream	< 0.003	2	0.25	Aquatic Moss 0.6	none

TABLE 69.
COPPER BASIN, TENNESSEE
THALLIUM -- ppm

	Sediments
Controls	0.1
Mine Waste	0.25
Mill tailings in pond	1.4
Ocoee River below at Rogers Bridge	0.5

iron pyrite. In addition to any small amount of heavy metals in the original biomass of the coal swamp, as groundwater slowly circulates through the sediment mass, the reducing effect of the coal traps metal ions as sulfides. The more deeply buried the coal, the more pyrite (FeS_2) and other sulfides crystallize within the fossil biomass and the greater the trapping potential for heavy metals. The sequence of burial changes that occur in coal can be expressed in the fixed-to-volatile carbon ratio, essentially the graphite present relative to the amount of hydrocarbons (organic precursors decay relatively rapidly to stable hydrocarbons and CO_2). These metamorphic changes are the result of increased temperature at depth. Therefore, anthracites are most likely to contain significant metal concentrations. When this coal is burned at power plants, any Tl present can become concentrated in electrically-precipitated fly ash. Power plants using this type of coal are now restricted to the original mining district from the Lehigh River to Scranton, Pennsylvania. Up to 76 ppm of thallium has been reported in flyash (Natusch, Wallace and Evans, 1974).

On the basis of these arguments, the anthracite region of Pennsylvania was selected for study of the heavy metal hazard in fuel burning. Unfortunately, exhaustion of these coal deposits has caused closing of almost all anthracite-burning operations. Electric powerplants are identified in Table 70. All but the standby plant at Harding were sampled. No other large anthracite-consuming processes were found in use locally.

Ash from the closed power plant in Nesquehoning Creek contained 47 ppm zinc, 37 ppm copper, 0.51 ppm lead, 21 ppb cadmium, but no measurable thallium. Strip mine tailings in the immediate vicinity contained comparable amounts of heavy metals. Flyash from the abandoned Glen Alden power plant on the Susquehanna River contained 64 ppm zinc, 123 ppm copper, 2 ppm lead, 0.26 ppm cadmium and no measurable thallium.

Mine-run coal contains larger amounts of waste each year, and the convenient surface area available for disposal becomes less. Huge mountainous piles of waste fill the coal-bearing valleys. In the narrow southern valleys, conveyors pour the waste over the rimrock and down into the surrounding unpolluted wooded plateau. The fine tailings of silt or 'slush' have also been deposited in huge unstable piles to avoid the final cost of returning it underground or to fill strip-mine pits. The mud eroded from the mound of waste at Port Blanchard contained 170 ppm zinc, 40 ppm copper, 0.41 ppm lead and 77 ppb cadmium.

TABLE 70.

ANTHRACITE BURNING POWERPLANTS

STANDBY	PENNSYLVANIA POWER & LIGHT CO.	AT HARDING ON SUSQUEHANNA RIVER
CLOSED	" " " "	" HAUTO DAM ON NESQUEHONING CREEK
RUINED	GLEN ALDEN COAL CO.	AT NANTICOKE ON SUSQUEHANNA RIVER
	OLYPHANT	AT DICKSON CITY ON LACKAWANNA RIVER
BURIAL UNDER WASTE	JENKINS	AT PORT BLANCHARD ON SUSQUEHANNA RIVER

As much as 40 tons of water were dumped from the mines into streams to recover each ton of coal. The streams draining waste and strip areas were acid and dead. Particularly dirty stream water from Taylor, southwest of Scranton, was sampled as well as sediment from several waste ponds and streams. The water contained 71 ppb copper and 80 ppb zinc. No cadmium, lead or thallium were detected.

All of the data indicate that coal mining and burning could contribute significant quantities of toxic lead and cadmium to the environment by flood erosion. However, no measurable thallium quantities would be contributed.

Bituminous Burning Plants

For comparative purposes, a bituminous coal-fired power plant at East Corning, New York, was sampled. The plant is on the Chemung River, a large swift Appalachian Stream with a steep gradient and coarse alluvial bed.

The river water and bed were sampled immediately above and below the plant. Fine sediment and benthos (algae, mayfly larvae and miscellaneous forms) were obtained from beneath many boulders. Fish, including minnows and foot-long suckers and giant shiners, were netted by hand from swift, shallow riffles.

A fly ash pond, approximately 100 yds. from the river bank and backwater, was sampled to determine the variability of the fine metalliferous waste. This material erodes into the Chemung River as a result of rainfall and washwater leaching. Smartweed (Equisitum), and poplar (Populus) seedlings were found growing close to the fly ash pond. The recent flood, which did even more serious damage in the Anthracite Coal District, washed out the Corning city sewage treatment plant just above our sample sites. In addition to increasing upstream pollution, the flood washed away everything around the powerplant including much flyash and its treatment system.

Results of heavy metal analyses for water, sediment, and biota samples are tabulated in Tables 71 and 72. Although significant thallium was found in sediments and biota, none was detected in water samples. The data suggests that bituminous coal pyrites do not contain enough Tl to provide an environmental threat. The heavy metals, cadmium, copper, lead and zinc, were found in sediments, biota and water. Levels of cadmium and lead in

TABLE 71.

CORNING WATER SAMPLE ANALYSES*

	Cd (ppm)	Cu (ppm)	Pb (ppm)	Zn (ppm)
Downstream river water	0.017± 0.002	0.009±0.002	0.13±0.01	0.035±0.004
Upstream river water	0.015±0.002	0.007±0.002	0.084±0.008	0.015±0.002
Upstream river water	0.018±0.002	0.005±0.002	0.10±0.01	0.010±0.001
Upstream river water	0.022±0.002	0.006±0.002	0.12±0.01	0.018±0.002
Fly Ash Pond	0.018±0.002		0.23±0.02	0.14±0.01
Fly Ash Pond (duplicate)	0.10±0.01	0.11±0.01	0.27±0.03	0.14±0.01
Fly Ash Pond (triplicate)	0.017±0.002	0.031±0.003	0.14±0.1	0.048±0.005
	<0.002	0.002±0.002	<0.002	<0.002

No thallium was detectable in water samples

*VARIATIONS SHOWN ARE ESTIMATED ANALYTICAL ERRORS FROM VARIATIONS IN STANDARD SIGNAL LEVELS.

TABLE 72.
CORNING SEDIMENT, VEGETATION AND BIOTA SAMPLES (CONC. IN PPM)

	Cu	Pb	Tl	Zn
Flyash pond:				
Horsetails	27±3	23±2	< 2	39±4
Poplar	29±3	20±2	1±1	67±7
Grass-leaves	22±2	18±2	< 1.2	32±3
Grass-roots	16±2	40±5	1.6±0.9	11±1
Grass-leaves & roots	29±3	11±1	< 1.3	28±4
Helianthus	18±2	2.1±0.8	1.5±0.8	26±3
Fine sediment	20±2	21±2	1	120±10
Find sediment (duplicate)	14±1			22±2
Coal	28±3	1.	1.9±0.9	63±6
Septic sediment	29±3		6.2±1	
Cladophora	8.2±0.8	12±1		30±3
Coarse sediment	13±1	2.2±0.4		26±3

river water both upstream and downstream of the flyash pond exceeded recommended EPA drinking water standards (EPA lead limit-0.05 mg/l; cadmium limit-0.10 mg/l). The data indicate that the flyash pond could be a source of cadmium and lead discharges to the river.

SECTION VI

DISCUSSION

The ecology of most of the trace metals measured in this study (copper, zinc, lead and cadmium) have been discussed previously Their known biological and geochemical balances are reasonably well supported by the data in this report. Thallium (along with some data on indium), however, have rarely been studied and will be considered in more detail.

Abundance and Distribution of Thallium

There is approximately 1 gram of thallium (Tl) per ton of the earth's crust. This is one-tenth the abundance of lead and 1/300 that of copper and zinc. Thallium is strongly concentrated in igneous and volcanic rocks (Sargent, 1952).

Significant amounts of Tl are concentrated in the high temperature sulfide metal deposits of volcanic terrains. In the United States, these are bodies that are restricted to Alaska, the western Cordilleran mountain states, and the Appalachians. Although the distribution of Tl within such ores is variable, depending on the composition of the mineralizing solutions, country rock, and geothermal gradient; it has been possible to indicate which industrial plants present the greatest Tl hazard as long as volcanic-origin ores are processed.

Tl is usually associated with sulfide concentrations of zinc (Zn), lead (Pb), copper (Cu), iron (Fe), cadmium (Cd), arsenic (As), indium (In), selenium (Se), and tellurium (Te). The overt mineralization of Tl is summarized in Table 73. The solutions, minerals and equilibrium of Tl deposition with Cd, Zn, Cu, and Fe can be visualized by means of the Eh-pH diagram, a plot of reduction-oxidation potential versus acidity (see Figure 39). The appropriate Eh versus pH field depicts the equilibrium thermodynamic conditions under which Tl can exist in solutions and solids.

The Eh-pH ranges of Tl deposition are shown as the shaded area in Figure 39. Depositions from hot brine (H_2O) occur in the field including Tl and Chalcopyrite ($CuFeS_2$), pyrite (FeS_2), and galena (PbS) but not magnetite (Fe_3O_4) or chalcocite (Cu_2S). Eh-pH diagrams are available for the systems Cu-Fe-S-O-H and Pb-S-CO_2-O-H, shown superposed in Figure 39. The deposition of Tl is confined to the FeS_2 field. Zn and Cd are similar to Pb.

TABLE 73. THALLIUM MINERALS

Name	Chemical Composition	Occurrence
Crookesite	(Cu, Tl, Ag)$_2$ Se	a variety of silver glance Ag_2S
Lorandite	Tl As S_2	with AsS
Hutchinsonite	(Tl, Ag)$_2$ S · PbS · 2 As_2S_3	in dolomite Mg Ca $(CO_3)_2$
Vrbaite	Tl, As_2 Sb S_5	with AsS and As_2S_3

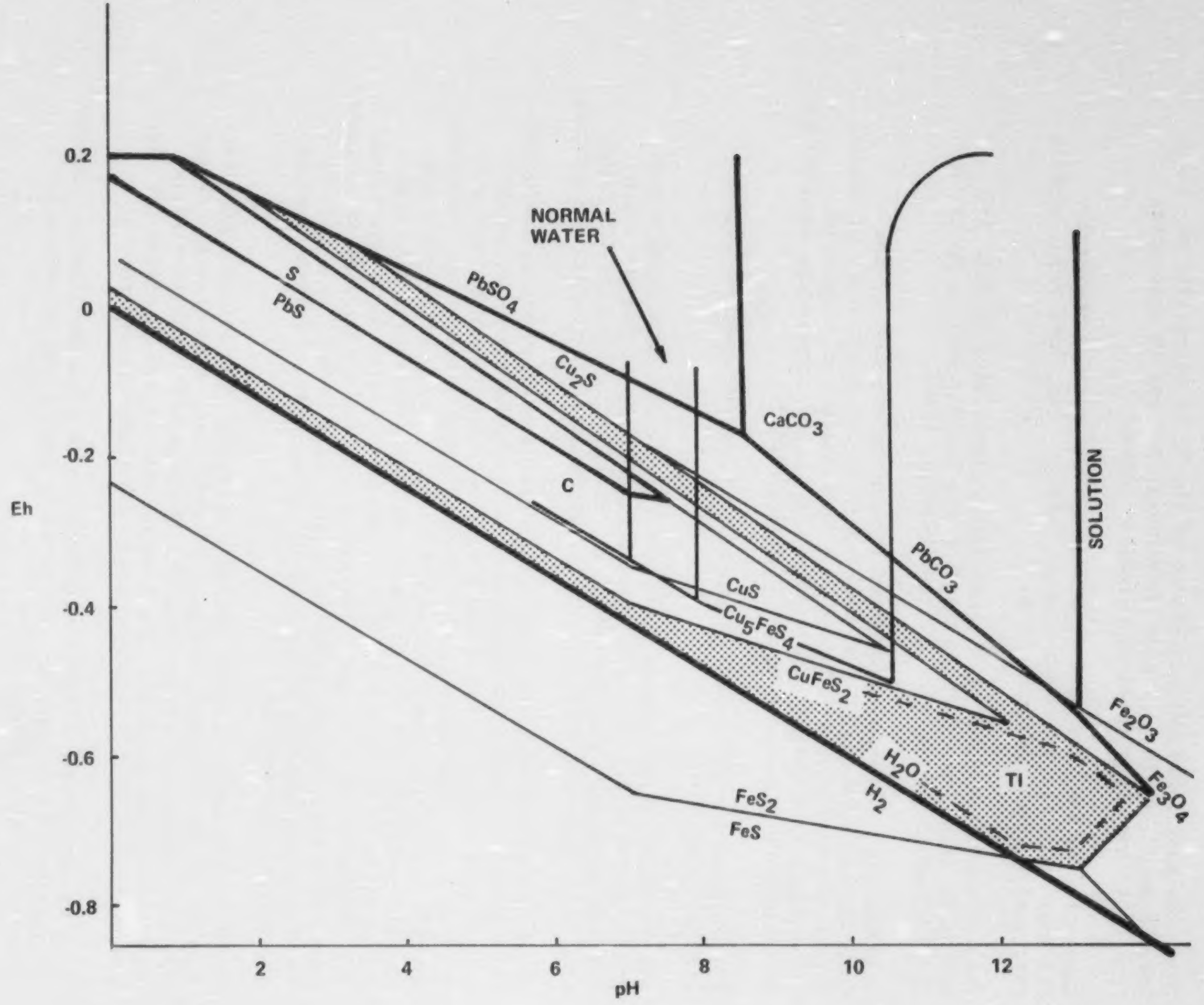

FIGURE 39. CHEMICAL ENVIRONMENTS OF METAL DEPOSITION

Thus, the most important occurrence of the Tl is in pyrite, or "fool's gold", which is almost universally present in base-metal ores, coal and other chemically-reduced rocks.

Copper is, by far, the most important sulfide metal commercially. Its most important ore, Chalcopyrite ($CuFeS_2$) can, like FeS_2, contain relatively large quantities of Tl.

The western mines occur in a trend from Arizona through Utah and Nevada to Butte, Montana, paralleling the Pacific Coast. Up to 5% Tl is found in cupriferous pyrites (Gmelin, 1938).

Lead and zinc are found associated with or to the east of the Cordilleran copper belt. The more easterly occurrences are of colder origin and tend to contain less Tl. The zonation of commercial major metal from west to east (from high to low temperature deposition) is roughly Fe-Cu-Au-Ag-W-Mo-Zn-Pb (Brown, 1969).

The forms of the trace metals found in mining and smelting wastes are indicated below.

The tailings, which contain most of the pollution from metal mining, are mineralogically the same (primarily sulfide) as the ore which has been concentrated. Smelter slag, however, is fayalite (Fe_2SiO_4) with other unrecovered heavy metals substituted for iron in the lattice.

The major precipitant for toxic metals in natural waters is carbonate. The beneficial effect of carbonate alkalinity for removing soluble metals from water is particularly well-demonstrated in the Missouri lead belt, particularly Strother Creek which receives large quantities of mill and smelter lead discharges (5 ppm in mill water, 1550 ppm in mill sediments and 10,500 ppm in smelter sediments). The high carbonate bedrock in the Strother Creek precipitates lead effectively from the water to 0.27 ppm. The tie up of lead and cadmium in sediments does not prevent uptake by biota in this case however as evidenced by high concentrations of lead in larvae and crayfish which feed on the metal-laden detritus.

As discussed under analytic methods, chloride ions form a significant control to the solution transport of thallium. A particular halogen complex (ligand) is formed with the thallous ion which is readily adsorped or precipitated. The loss of this ligand is similar to the precipitation of thallium with bromine outlined in Appendix B.

Sulfate ions have a slight solubilizing effect on thallium as compared to nitrate ions at constant pH, probably due to the oxidation of some Tl^+ to more soluble Tl^{+++}.

Chelation by dissolved organic substances may be an important mechanism, in addition to the thallous chloride complex and adsorption on particulate matter, particularly in suspended clays with their enormous surface area. This is especially true in streams like the South Fork of the Coeur d' Alene saturated in untreated sewage. The organic ligands generally tend to increase metal solubility, in contrast to the chloride precipitation effect.

Behavior of Thallium in Natural Waters

The chemistry of thallium in natural waters has some puzzling features. The most obvious is the discrepancy between the relative abundance in soils (typically up to 10 ppm in those derived from granite crust) and the rarity in sea water (normally less than .01 parts/billion as reported by Golberg, 1962). The atomic radius of Tl^+ is 1.44 angstroms making the density relatively low so that Tl is carried into stack gas where it is easily precipitated electrically. Up to 9% Tl has been found in flue dusts (Sargent, 1953). Soil thallium is derived from orthoclase, the common potash feldspar where Tl^+ may readily substitute for K^+ in the lattice because of comparable atomic size, 1.44 vs 1.33 angstroms, respectively.

Thallium Exchange with a Montmorillonite Clay

It was hypothesized that the substitution of thallium for other metallic cations may take place in the montmorillonite clays, which if true, could be a significant factor in minimizing thallium movement in the environment. To check this hypothesis, a series of experiments was designed in which a montmorillonitic clay (hectorite) was chosen to determine the extent of preference of exchange of the thallous ion compared to potassium and to other ions such as copper and zinc.

Montmorillonite is the principal clay mineral of bentonite beds which originates from altered volcanic ash. Montmorillonite minerals are common as alteration products of igneous and metamorphic rock minerals in an alkaline environment with little leaching (e.g., arid climates). The western U.S. Rocky Mountain region has an abundance of montmorillonite in its soils. There are different species in the montmorillonite group and they vary in the type and degree of isomorphous lattice substitution rather than in structure. In this study, the montmorillonite called hectorite (hectorite #34 - API reference standard) was used. This mineral is one in which the principal substitutions are octahedral and has a general structural formula of

$$(Al_{.01}\ Li_{.30}\ Mg_{2.67})\quad (Si_4)\ O_{10}\ (OH)_2$$

In the presence of water, the cations in the interlayer positions may be easily exchanged with other cations when available in solution. Isomorphous substitution results in charge deficiency which may occur in the octahedral or tetrahedral layer. The charge deficiencies can be neutralized by exchangeable cations so that the mineral becomes electrically neutral. Therefore, exchange may occur not only by cations in the interlayer position, but into layers of the lattice as well.

Experimental

Ten and one grams samples of hectorite per liter distilled water were prepared containing 1000, 100 and 10 µg/l of thallium (I), copper (II) and zinc (II). The pH of the solution of hectorite and water was adjusted to four and approximately eight with dilute sulfuric acid prior to the addition of metals. The clay slurry was continually agitated for 24 hours to achieve good contact between the clay and metal ions in solution. After the contact period, clay was removed by settling and centrifuging to obtain a clear liquid prior to extraction and atomic absorption analysis.

The liquid, free of clay, was extracted with DDC (diethyldithiocarbamate) to concentrate the metal ions. Thallium analysis was performed using a heated graphite atomizer whereas copper and zinc were aspirated directly.

Blank samples without hectorite and hectorite solutions without metals were prepared to assure no interferences or metal losses.

Results

Three separate experiments were carried out using hectorite, potassium treated hectorite, thallium, copper and zinc in various concentrations. Ten grams of hectorite per liter of water with different concentrations of thallium, copper and zinc at two pH levels (4.0 and 8.2) revealed more efficient take-up of metal ions in basic solution (see Table 74).

At pH 8.2 the thallium concentration was reduced from 1000 µg/l to 25 µg/l. Copper and zinc were reduced from 1000 µg/l to <10 µg/l Other concentrations of Tl, Cu and Zn were reduced to below their detectability limit.

TABLE 74

EXCHANGE CAPACITY OF HECTORITE
WITH THALLIUM, COPPER AND ZINC (10 g/liter Hectorite)

	Initial			Final		
pH	Tl µg/l	Cu µg/l	Zn µg/l	Tl µg/l	Cu µg/l	Zn µg/l
8.2	1000	1000	1000	25	< 10	< 10
8.2	100	100	100	< 3	< 10	< 10
8.2	10	10	10	< 1	< 10	< 10
8.2	0	0	0	< 1	< 10	< 10
4.0	1000	1000	1000	900	562	619
4.0	100	100	100	3	29	10
4.0	10	10	10	< 1	< 10	< 10
4.0	0	0	0	< 1	< 10	< 10

In acidic solution (pH 4.0) metal reduction in solution was not as pronounced as in basic solution. Initial 1,000 µg levels of Tl, Cu and Zn were reduced to 900, 562, and 619 µg/l, respectively. Concentration of metals at 100 µg/l also did not reduce as dramatically as in basic solution but did adsorb in greater proportion than the 1000 µg/l metal sample at the same pH value.

An experiment was performed in which the concentration of clay was changed from ten grams of hectorite per liter to one gram of hectorite per liter of solution at a pH of 8.1 (Table 75). Initial concentrations of Tl, Cu and Zn of 1000 µg/l were reduced to 115, 270 and 511 µg/l. Other concentrations of metals (100 and 10 µg/l) were reduced near or below their detectable limit.

When hectorite initially is saturated with 2000 µg/l potassium, the rate of exchange for thallium is only slightly affected (Table 76), a reduction of 1000 to 25 µg/l was obtained without potassium ions and a

TABLE 75

EXCHANGE CAPACITY OF HECTORITE WITH THALLIUM, COPPER AND ZINC
(1 g/liter Hectorite)

	Initial			Final		
pH	Tl µg/l	Cu µg/l	Zn µg/l	Tl µg/l	Cu µg/l	Zn µg/l
8.1	1000	1000	1000	115	270	511
8.1	100	100	100	3	< 10	< 10
8.1	10	10	10	< 1	< 10	< 10
8.1	0	0	0	< 1	< 10	< 10

TABLE 76

EXCHANGE CAPACITY OF POTASSIUM-TREATED HECTORITE WITH THALLIUM, COPPER AND ZINC

	Initial				Final		
pH	K µg/l	Tl µg/l	Cu µg/l	Zn µg/l	Tl µg/l	Cu µg/l	Zn µg/l
8.2	2000	1000	1000	1000	90	< 10	< 10
8.2	2000	100	100	100	3	< 10	< 10
8.2	2000	10	10	10	< 1	< 10	< 10
8.2	2000	0	0	0	< 1	< 10	< 10

reduction of 1000 to 90 µg/l in a potassium treated clay. The concentrations of copper and zinc in solutions of clay saturated with and without potassium ion were reduced to below their detectability.

Conclusions

The experimental results show that thallium ions can be removed effectively from solution by a montmorillonite clay. Greater removal of thallium is achieved inslightly basic waters versus slightly acidic waters. This may be due to the increased solubility of the metallic ion in the acidic media. Other metal ions, specifically copper and zinc also follow the same trend. Clays, saturated with potassium ions, show only slight differences to clay that had not been treated with potassium ions.

The disappearance of thallium from less-acid waters may be related to reduction of unstable Tl^{+++} (thallic) to Tl^{+} (thallous) ions and subsequent ion-exchange with suspended clay. This mechanism is quite efficient, and there is little biological uptake of thallium. However, organic complexes such as those formed with MIBK are known on analysis and may persist through the food chain despite their toxicity. The general path of thallium from water through biota is shown in Fig. 40. A good example is the South Fork of the Coeur d' Alene mentioned above (Table 14).

The metal fractionation between water and sediment can be understood in terms of the solubility of the available salts of the metal ions found (Table 77). Tl, like Pb, accumulates from acid water in neutral or alkaline sediments, especially fine muds.

Biology

The relations of the more toxic metal (Tl, Cd, Pb) concentrations in each trophic level of the biota to its sediment and water concentrations are plotted in Figures 41-44. Data from all sampled sites are included. The concentration of metal in the biota was found to be more closely related to the concentration in its bottom sediment than to its water except for a few floating algal slimes surviving above lead-rich mud, particularly at East Helena. Toxic water discharges can occur sporadically, leaving a record in the sediment. Benthic organisms were found generally to accumulate more than fish.

In the following discussion, prior observations (Hager, 1971) for each metal are summarized for comparison with the data collected in this study. The average concentration of cadmium found in rivers

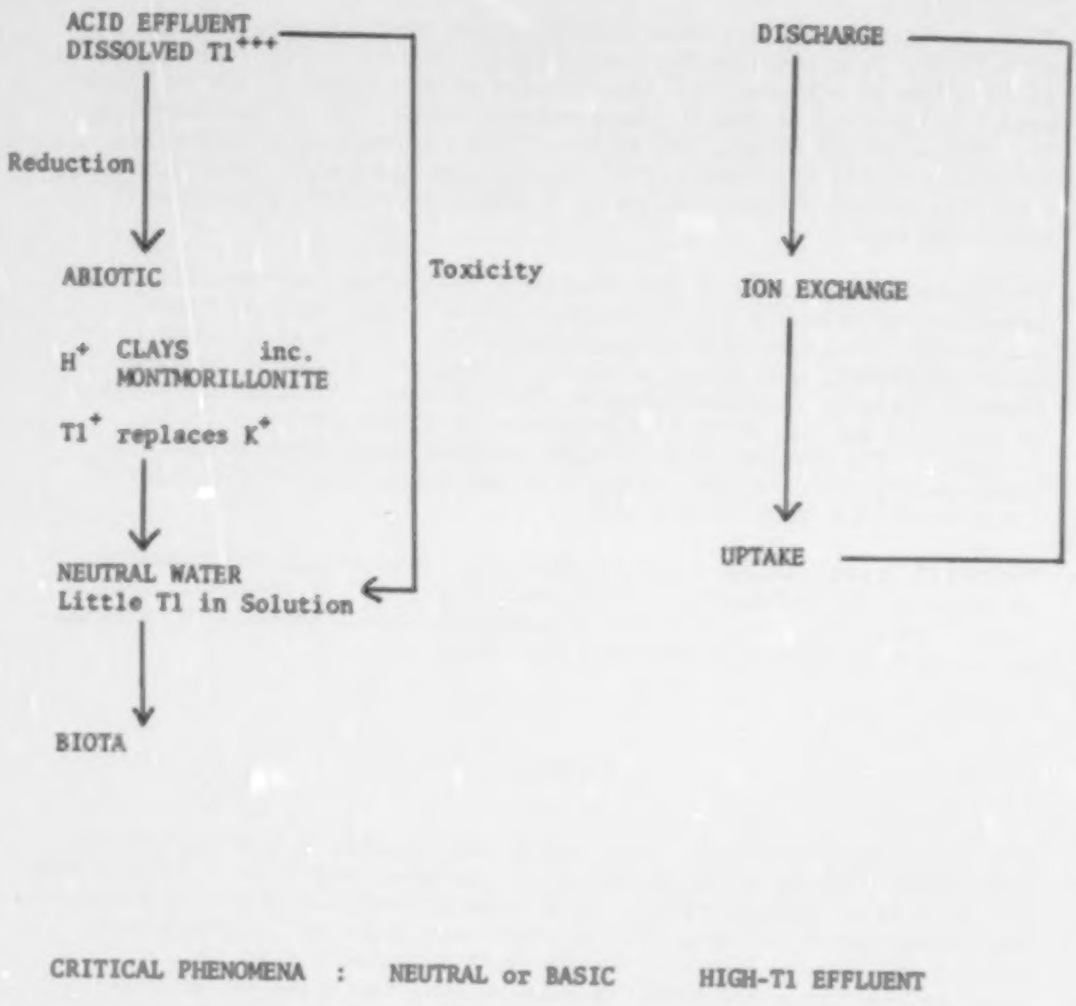

FIGURE 40. GENERAL PATH OF THALLIUM FROM WATER THROUGH BIOTA

TABLE 77

SALT SOLUBILITIES IN WATER

	Cl^-	$SO_4^=$	$CO_3^=$	$S^=$
Tl^{+++}	86%	decomposes to $+2SO_2 + H_2O$ Tl_2SO_4	decomposes to Tl_2CO_3 $+ CO_2 + H_2O$	not found
Tl^+	0.32%	4.9%	4%	0.02%
Cd^{++}	140%	76%*	ppm range	13 ppm
Pb^{++}	0.07-0.99%	26-42 ppm	1.1-1.7 ppm	0.0 ppb
Cu^{++}	71%*	decomposes to Cu_2SO_4	not found	0.33 ppm
Cu^+	62 ppm	14%*	1.5 ppm	10^{-16}
Zn^{++}	432	86	0.001	0.65 ppm
pH 7 at 20°C unless *at 0°C				

by Hager was 0.24 ppb but only 0.11 ppb in seawater. The average in concentration of lead in rivers is now 4.2 ppb and 0.3 ppb in surface seawater primarily due to leaded gasoline. Deeper seawater contains only 0.03 ppb. Toxicity is cumulative and varies from 100 ppb for oysters to 4 ppm for fish. The average concentration of copper in rivers is 10 ppb, about as much as in nearshore seawater. Copper is toxic to algae at approximately 25 ppb although fish can tolerate 30 ppm. The average concentration of zinc in rivers is 10 ppb and up to 15 to 20 ppb in seawater. Aquatic toxicity of zinc requires 5-10 ppm. Marine plankton can concentrate heavy metals at factors which can vary from 910 for cadmium, 4100 for lead, and 20,000 for zinc (Hager, 1971).

The higher trophic levels sampled in this study, especially larvae and fish, were found to have lower concentrations of toxic metals than lower trophic levels (algae). We believe this is due to a combination of factors including feeding on uncontaminated detritus, mobility and biochemical rejection mechanisms.

This agrees with Merlini *et al*. (1971) who showed copper concentrations of 2.2 ppm in Lake Maggiore algae (*Myriophyllium*) but only 0.9 ppm in small fish (*Alburius*) and 0.5 ppm in large fish (*Coregorus*, *Scardinius*). Zinc decreased from 20 ppm in algae to 4-8 ppm in large fish.

Unlike methyl mercury, thallium and other toxic heavy metals showed little increase in concentration up the food chain. Sulfide precipitation removes these readily reduced cations, concentrating them in black organic oozes.

The graphs (Figures 41-44) summarize the research in showing that there was little bioconcentration from water.

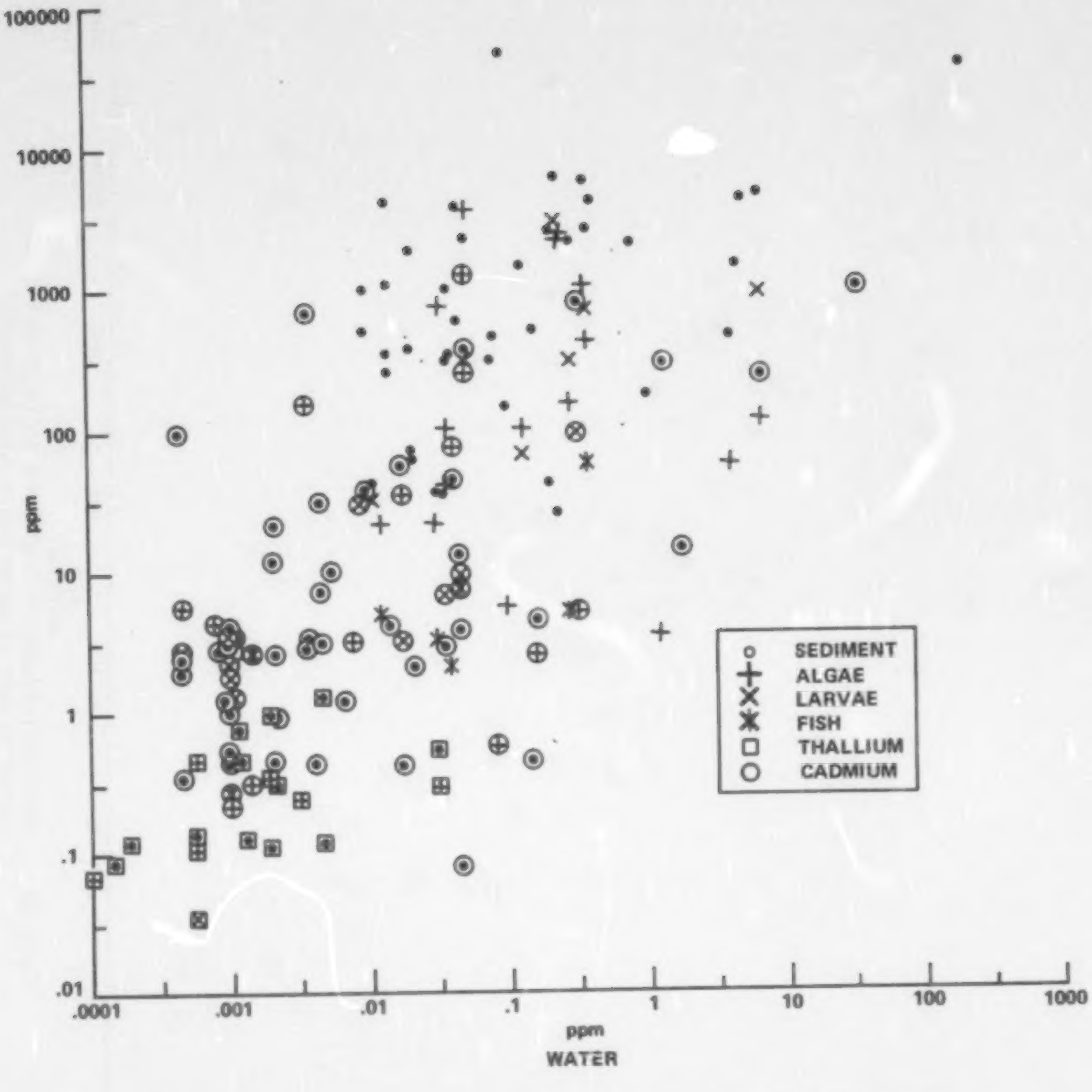

Figure 41 CONCENTRATION OF THE TOXIC METALS THALLIUM, CADMIUM, & LEAD IN BIOTA, SEDIMENT & WATER

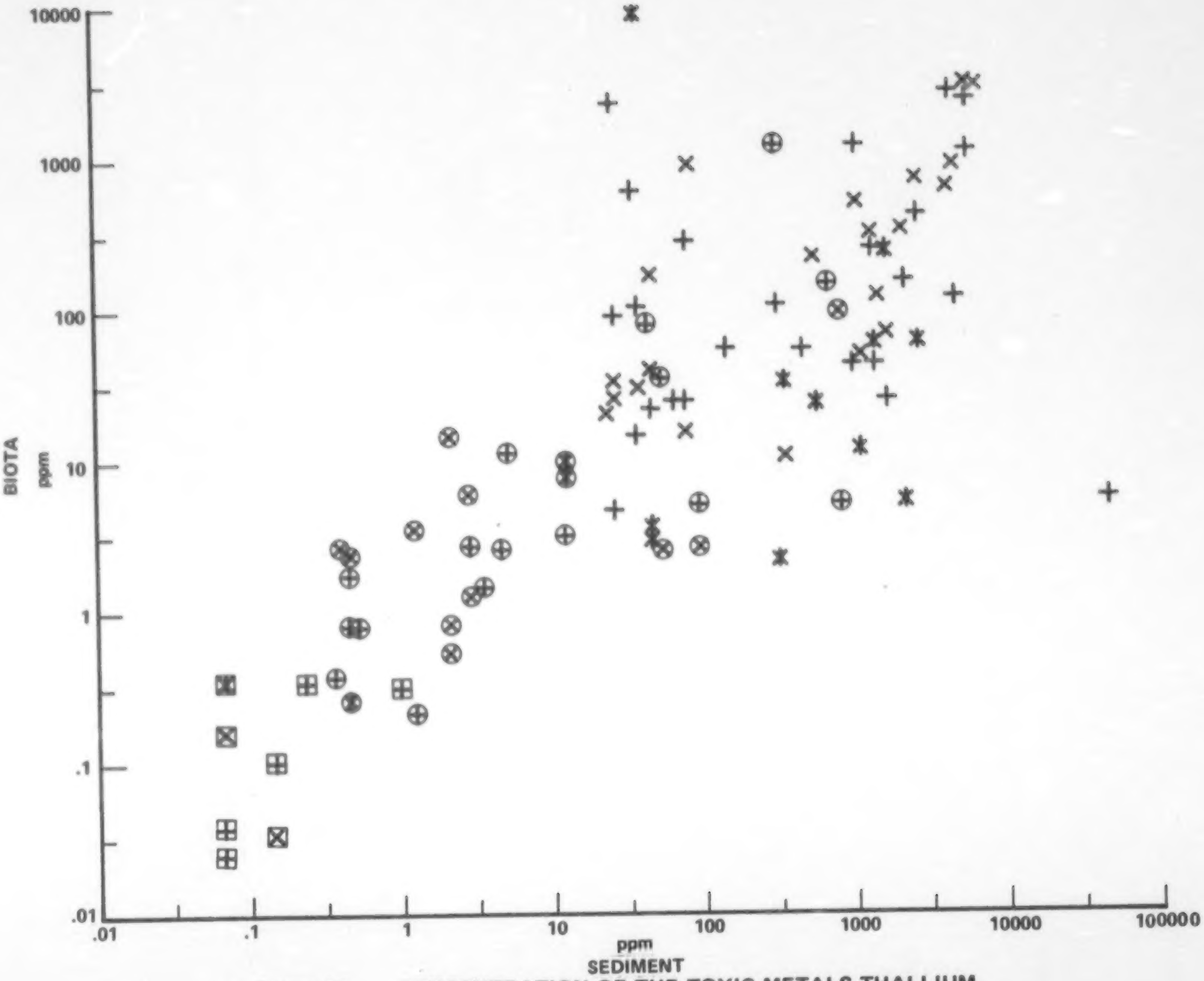

Figure 42 CONCENTRATION OF THE TOXIC METALS THALLIUM, CADMIUM AND LEAD IN BIOTA AND SEDIMENT

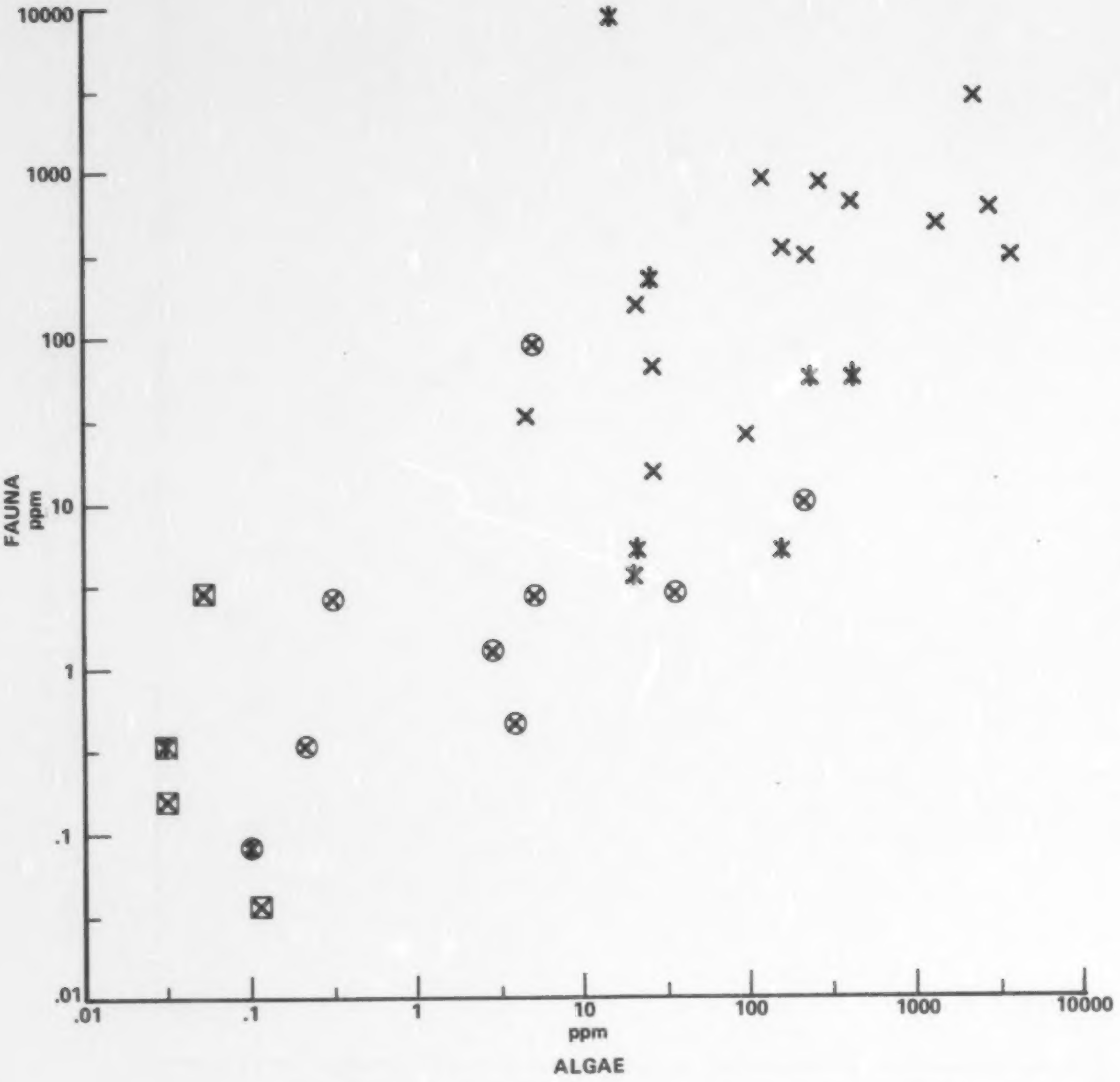

Figure 43 CONCENTRATION OF THE TOXIC METALS OF THALLIUM, CADMIUM & LEAD IN FAUNA AND ALGAE

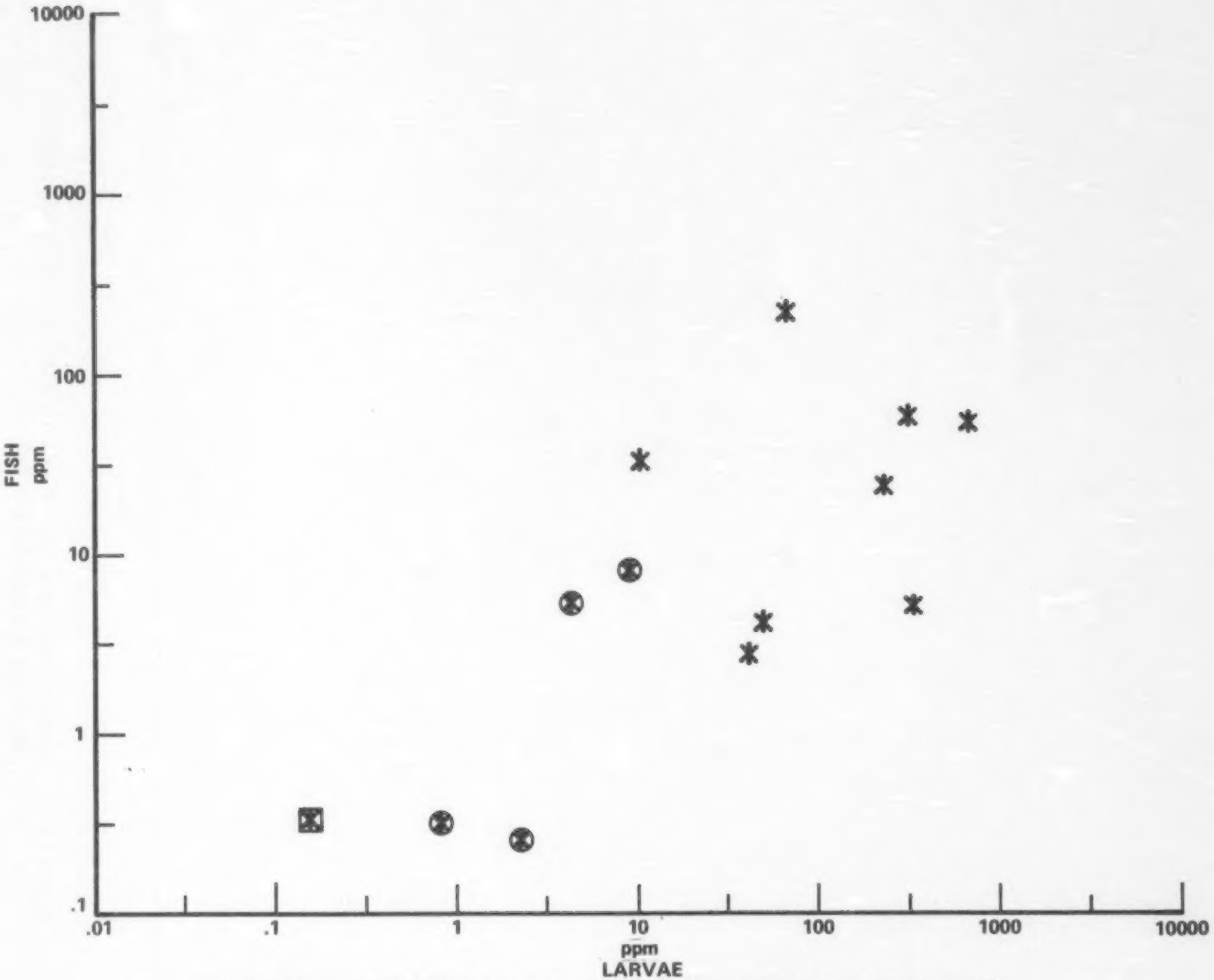

Figure 44 CONCENTRATION OF THE TOXIC METALS OF THALLIUM, CADMIUM & LEAD IN FISH & LARVAE

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APPENDIX A

STUDY OF ALTERNATE SAMPLE PREPARATION METHODS

Sediment and biological samples must first be solubilized before analysis by atomic absorption spectrophotometry, the analytical method used in this project. Sediments can be digested with perchloric, sulfuric, and phosphoric acids, but care must be taken not to volatilize elements of interest including Tl, Pb, Cd, Zn, As, Cd and Cu. Table 4 shown previously in Section IV gives data on volatilization losses of various heavy metals using the aforementioned acids, but care must be exercised when analyses of other metals in the same sample are desired.

Five methods for achieving the solution of metals from sediment and sludge samples were originally investigated. It was expected that an extraction technique which would allow reliable analysis of both of these samples would work for all soil samples. The five methods studied are outlined below.

1. Pressure digestion -- 5 grams of sample digested with 1.5 gms $HClO_4$ + 3.5 gms HNO_3 in a closed bottle -- overnight at room temperature -- then 2-3 hours in running hot water -- cool, dilute and analyze.

2. Room temperature extraction -- 5 gms soil extracted with 10 ml HNO_3 + 15 ml HCl at room temperature -- contact time ∽ 72 hours with occasional mixing.

3. 0.2 gms soil + 15 ml HCl + 10 ml HNO_3 heated and evaporated to dryness. Dissolve soluble residue in 5 ml hot HCl dilute with H_2O.

4. 0.2 gms soil + 15 ml HCl + 5 ml HNO_3 boiled 10 15 minutes--cooled--diluted with H_2O.

5. Room temperature extraction--5 gms soil extracted with 10 ml HNO_3 at room temperature ∽ 72 hours with occasional mixing.

Two portions of each sample were extracted by each technique to provide a measure of the reproducibility of the analytical results.

Results of the analysis are summarized in Table A-1 below, where an average for each soil sample and for each analytic technique are presented. The number of samples analyzed and the number used in determining the average values differ in several cases because samples in which something was known to have gone wrong in processing were not included in the calculation of the average nor in determining the root mean square variations.

Straight acid treatment (HNO_3 + HCl) of water and sediment samples followed by aspiration by conventional means into an atomic adsorption spectrometer produced varying results. Standard samples containing known concentrations of thallium (as the nitrate) can be easily analyzed yielding interpretable results and calibration curves. At times, levels of thallium were "observed" to be present, but slight changes in burner conditions remove the thallium signal. In each case where a response for thallium was observed the emissions from other materials also in the sample were extremely high. Ordinarily such emissions, if at moderate levels, can be compensated for with an emissions correction device. Many of the emissions encountered are beyond the capability of this corrector. Dilution of the sample to reduce emissions resulted in completely removing the previously observed thallium signal. In some cases, no signal was obtained. Since direct aspiration of acidified samples leave the thallium concentration in doubt or highly questionable, other modes of sample work-up and instrumental variations using atomic absorption were deemed necessary.

A heated graphite atomizer (HGA) was used to eliminate flame effects and to increase sensitivity. Thallium standards were introduced into the HGA and produced sensitivities ten times that by aspiration. A series of samples were introduced into the HGA in the same mode as the thallium standards but no signlas were observed.

TABLE A-1.

ANALYTIC RESULTS (in ppm)

		Cd	Cu	Pb	Ti	Zn
Sample #6						
Avg		184	$2.2x10^4$	2897	3.1	1720
Procedure 1	(2 samples)	180	$2.3x10^4$	1170	1.7	2080
2	"	200	$2.1x10^4$	2933	3.6	1900
3	"	163	$2.2x10^4$	3016	No det	1650
4	"	163	$2.3x10^4$	3140	No det	1608
5	"	200	$2.0x10^4$	2580	2.8	1800
No. of Samples		10	10	10	6	10
No. Samples in Avg		7	7	7	4	7
No. Measurements in Avg		7	14	12	5	10
rms Dev of Measurements		18.4	$0.19x10^4$	256	0.74	130
rms Dev. sample Avgs		18.4	$0.15x10^4$	219	0.75	125
Sample #4						
Avg		65	$5.0x10^4$	1400	7.0	416
Procedure 1	(2 samples)	67	$5.0x10^4$	1300	8.2	405
2	"	60	$5.1x10^4$	1480	5.2	410
3	(1 sample)	67	$4.8x10^4$	1450	No det	479
4	(1 sample)	69	$5.3x10^4$	1390	No det	405
5	(2 samples)	65	$4.8x10^4$	1410	7.4	380
No. of Samples		8	8	8	6	8
No. Samples in Avg		8	8	8	6	8
No. Measurements in Avg		8	15	16	9	10
rms Dev of Measurements		4.3	$0.38x10^4$	102	1.8	39
rms Dev of Sample Avgs		4.3	$0.25x10^4$	74	1.4	32

Addition of standards to the samples either in the field or in the laboratory resulted in strongly decreased responses or a complete quenching of the expected thallium signal. It was found on separate experimentation that chloride ions had a large quenching effect. Chloride is very abundant in nature, and all natural samples contain it to some degree. In addition, some of the samples of interest were essentially seawater.

Additions of silver nitrate to samples, as well as to synthetic standards containing thallium and chloride, precipitate the chloride ion as silver chloride. Removal of chloride from the samples did not remove the interference in natural samples. This indicated other components in the sample were still interfering.

Sulfide Precipitation

Attempts at isolating thallium from the sample matrix was the next step. Two types of thallium removal were tried; one to precipitate the thallium as the sulfide and the second to complex the thallium as an organic complex. Both techniques also remove other multivalent metal ions from solution, but ions such as K^+, Na^+, Cl^-, $SO_4^=$, etc., are left behind.

The sulfide procedure used was detailed in Table 3 of Section IV. Recovered thallium sulfide (Tl_2S) and other metal sulfides were redissolved in concentrated HNO_3, diluted 50% with distilled water, and aspirated directly into the AA burner. Comparison of standards with precipitated samples at the same concentration showed recoveries of approximately 90% thallium. This method appears reasonable for analyzing aqueous samples to a sensitivity of ~0.5 ppm Tl. The same samples were analyzed using the heated graphite atomizer (HGA) AA attachment, and the data obtained showed reduced signals for thallimm.

Organic Complexation

Organic complexation using diethyldithiocarbamate (DDC) and subsequent extraction (Table 2, Section IV) was performed on selected samples. Standards of thallium extracted adequately with a ~90% efficiency. These samples were analyzed by direct aspiration of the organic solvent. Extracted samples mainly show minimally detectable and questionable concentrations or zero response for thallium. Thallium added to samples showed quantitative recovery.

Organic complexation with DDC, extraction with MIBK (methyl isobutyl ketone), evaporation and solubilization in HNO_3 was the most promising technique investigated. Samples with their varied composition necessitate at least one addition of thallium to each sample to verify extraction efficiency. This is especially important with sediment samples where overall extraction efficiency has been shown to be only about 50%. The extraction procedure is time consuming and careful control has to be maintained to minimize losses. Possibly as many as 25 samples can be extracted per day by this method with optimized laboratory techniques. The instrumental response for thallium where detected in samples has been only a few times the noise level of the instrument. If a number of natural samples can be found that contain moderate amounts of thallium, conditions may be further optimized.

Sediment samples generally showed less recovery of thallium than the water samples. This may be due to the large amounts of other metals present also complexing with the DDC and reducing the DDC to thallium ratio, thereby leaving the thallium with little DDC available for complexation. The reduced signal may also be due to the large amounts of other extracted metals interfering with thallium.

Results of analyses for the biological samples indicated some problems with reproducibility of results. Differences larger than expected were found between the results of eight of twenty-five pairs of replicate analyses. These differences are due to plugging of the aspiration capillary, and may be eliminated by running samples twice or by more frequent standardization.

APPENDIX B

THALLIUM FIELD TEST KIT

A thallium test kit was field tested to check for the feasibility of testing thallium in the field. The lower limit of thallium detection was originally 0.5 ppm. A modification (Feigl, 1954) of the test kit was made allowing a detection of thallium to a level of 0.01 ppm.

The original test kit procedure involved the reaction of bromine to convert all thallous ions to thallic ions in solution. The excess bromine is then removed by adding sulfosalicylic acid. The dye rhodamine B reacts with thallic bromide to yield a violet rhodamine B - thallic bromide complex. If benzene is added, the thallic-rhodamine B complex is extracted yielding a fluorescent red benzene layer. Only antimony, gold and mercury interfere and these may be eliminated using special procedures.

The original test procedure involves only a few drops of test solution. In the modified procedures, concentration of thallium was performed by taking a large volume of test solution and treating it with freshly precipitated hydrous manganese dioxide. The manganese dioxide performs a collector action on thallium salts (like the effect of clay minerals in sediment and muddy water), and they precipitate together. The precipitate is then dissolved in a minimum amount of concentrated hydrochloric acid which is subjected to the rhodamine B test. The concentration of the thallium from the large volume of water lowers the overall limit of detectability to 0.01 ppm thallium.

The test procedure in step-by-step detail follows:

(1) 500 ml of aqueous solution is treated with 2 mg of manganese sulfate;

(2) Excess bromine water is added;

(3) Solution is made basic with 1 N NaOH;

(4) The solution after standing for 15 minutes is filtered through a 0.45 filter;

(5) The precipitate is dissolved in 2 ml of conc. HCl;

(6) Four drops of the HCl solution are diluted with four drops of distilled water;

(7) Excess bromine water is added (two drops);

(8) One drop of a 10% solution sulfosalicylic acid is added to destroy the excess bromine;

(9) Two drops of concentrated HCl are added;

(10) Two drops of 0.05% rhodamine B in concentrated HCl are then added and shaken;

(11) Eight drops of benzene are added and the solution again shaken;

(12) The benzene layer is observed under UV light for fluorescence;

(13) A rough scale of thallium concentration can be achieved by treating known concentrations of thallium in the same way as the unknown. A blank should always be run in parallel to any test. A difference in fluorescence of the sample over the blank confirms the presence of thallium.

The original test kit worked well using eye dropper fitted bottles and three inch test tubes. Field filtration of 500 mls of solution can be most conveniently performed using a 100 ml syringe with a two-way valve coupled to a millipore filter field monitor. The device eliminates the need for large amounts of filtration equipment in the field.

APPENDIX C

UPTAKE OF HEAVY METALS IN THE ULOTHRIX ALGAE

Some living organisms are capable of concentrating certain metals to an extreme extent. Stumm and Morgan (1970) have compiled data showing that plankton may show concentrations of up to 90,000 ppm for copper, 8,000 ppm for nickel; 12,000 ppm for lead; and 16,000 ppm for cobalt. Benthic algae show high concentration factors for nickel and manganese.

A sample of Cladophora from the Chemung River at Corning was found to have 12 ppm of lead. Rolfe et al (1972) reported that lead from vehicle exhaust accumulated in aquatic earthworms at a level of 370 ppm by dry weight.

The kinetics of copper, zinc, cadmium, lead, and thallium uptake by algae were investigated under controlled laboratory conditions by Dr. Kenneth Wood under a Calspan internal research program. This study has a significance to the heavy metal bioconcentration problem and is therefore reported here. The algae used in the study was a species of Ulothrix, common in winter and spring on rocky shores. It was collected from Lake Erie at Bart's Cove, Dunkirk, New York.

Procedures

The laboratory experiments were conducted in an artificial stream which contained two liters of water. Water was circulated between the stream and a gallon jar by means of a peristaltic pump. A constant flow of water thus bathed the algae, which were loose in the stream for all but a few experiments on thallium uptake.

It was decided to run a few experiments in which the algae would be contained within small permeable bags through which the thallium spiked water would flow. If results from uncontained and contained algae were close, this would give greater validity to field measurements in streams where the algae studied over a period of time would necessarily have to be contained in some way. The fabric bags (referred to as "tea bags") used in the laboratory tests and parallel testing in the Coeur d' Alene River, Kellogg, Idaho, and Silverbow Creek and Blacktail Creek, Butte, Montana, were made from dacron polyester with 10 mesh/cm (Figure C-1).

In both laboratory and field tests, approximately one gram of Ulothrix from Lake Erie were placed in bags.

The experiments were performed in several types of water, including Buffalo tap water, spring water, and algal culture medium. The trace element content of the unspiked water (no trace elements added) is shown in Table C-1.

The algal culture medium (minus trace metals) had the lowest background levels. The spring water was high in zinc (0.280 ppm) and in lead (1.400 ppm). Tap water often contained significant amounts of copper, zinc and lead. The use of various background levels of trace elements was an attempt to duplicate conditions that would be encountered during field use of the method.

After exposure to trace metals, the algae were harvested, weighed in a wet condition, and digested by a mixture of perchloric and nitric acids. Trace metals were then determined by atomic absorption analysis, either by aspiration into a flame, or in the heated graphite atomizer. The algae were found to contain 14 percent dry matter after drying one sample at 220°F.

Since the algae used in laboratory experiments were collected on a number of occasions from Dunkirk, it was necessary to ascertain if measured metal contents in lab experiments resulted from uptake from innoculated water or had accumulated in the algae while in the lake water. For this reason, metal contents of algae collected and used over the duration of the project (Feb.-April, 1973) were periodically measured. These measurements were used as controls and are tabulated in Table C-2.

The Dunkirk Harbor control algae showed wide variations in trace metal content. The highest concentrations occurred on February 6-8 at 185 ppm of copper and 215 ppm of zinc. High cadmium and lead concentrations were also found at this time. On March 7, 12.7 ppm of thallium was found in the control algae. A correlation between the concentration of metals in the experimental stream, and that found in the control algae is noted. In the experiment of February 6-8, concentrations of 0.1 to 1.0 ppm were used, and on

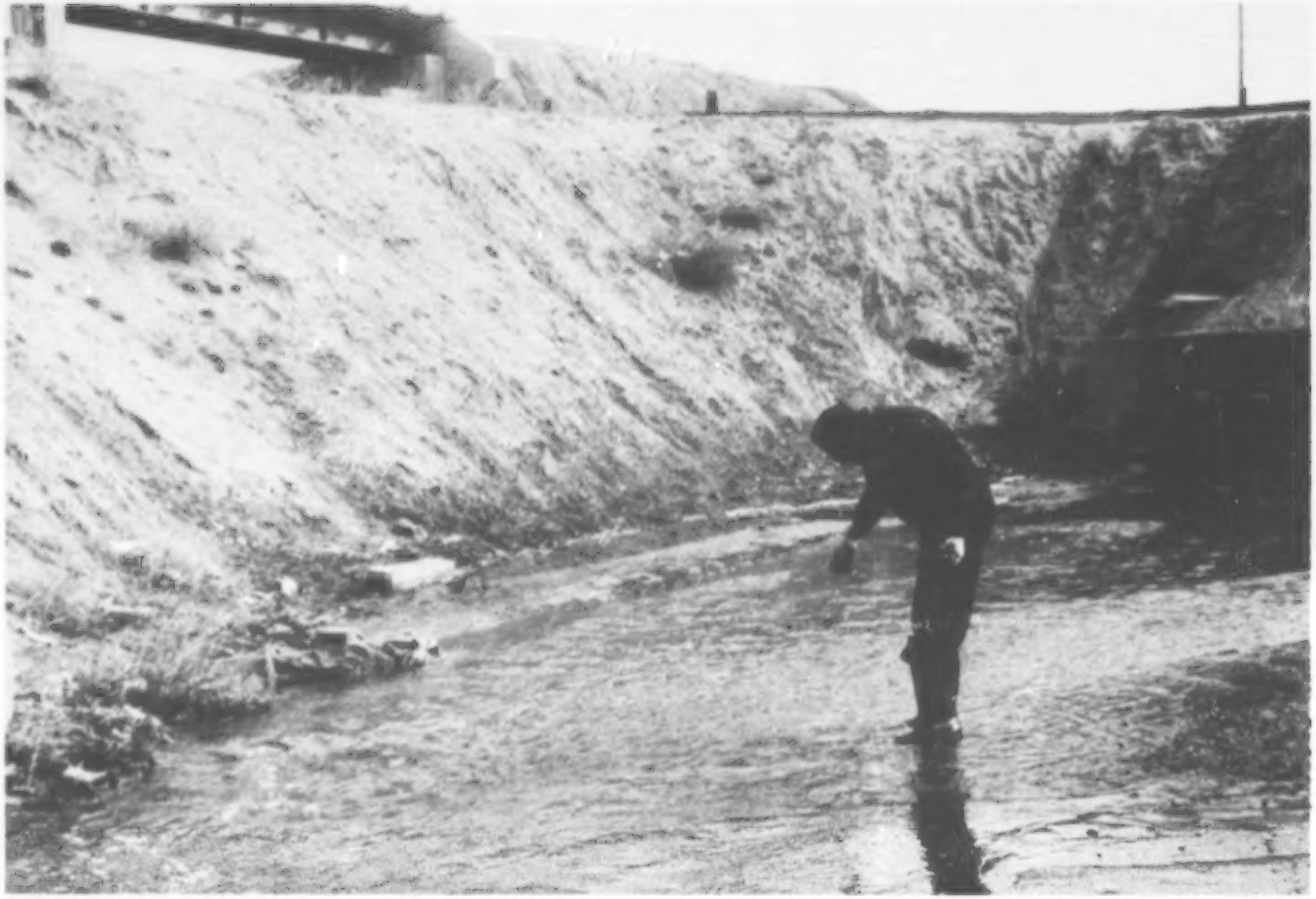

Figure C-1 TEST OF "TEA BAGS" IN SILVERBOW CREEK

TABLE C-1. Trace element content of control water samples.

1973 date	Source of Water	ppm Metals				
		Cu	Zn	Cd	Pb	Tl
2/6	Tap Water	0.200	0.170	0.120	0.490	--
2/6		0.050	0.110	<0.050	.050	--
2/8	" "	<0.050	0.050	<0.050	<0.050	--
3/1	" "	0.010	0.030	<0.001	<0.005	
3/1	Culture Medium & Trace Metals	0.023	0.018	0.0002	<0.0004	
3/5	Culture Medium	--	--	--	--	3
3/13	Spring Water	0.030	0.280	0.010	1.400	
4/4	Culture Medium	0.015	0.006	<0.005	<0.050	

TABLE C-2. Trace element content of control algae from Dunkirk Harbor in relation to date of collection.

1973 date	metals in control algae - ppm Cu	Zn	Cd	Pb	Tl
2/6	81	46	0.19	3.8	
2/8	185	215	0.78	<7.7	
3/1	6.8	1.2	<0.10	<0.2	
3/1	4.9	16.3	<0.10	<0.4	
3/3	23.5	17.6	0.20	<0.4	
3/5	--	--	--	--	0.42
3/7	--	--	--	--	12.70
3/7	--	--	--	--	0.13
3/13	0.1	0.7	0.03	4.7	
3/13	0.1	2.0	<0.03	4.4	
4/3	8.0	5.2	0.40	6.2	
4/3	6.0	4.4	0.45	4.0	
4/3	8.0	6.0	0.45	5.4	
4/3	20.0	7.4	0.80	7.8	
					<.3
5/15	3.6	13.3	0.33	<0.6	

March 7, 0.2 ppm of thallium was used. At other times, the experimental concentrations were $\sim$0.04 ppm. Intercontamination could have occurred during the experiment, during sampling, or during analysis. Therefore, the high concentrations for each metal were excluded in the calculation of average concentrations for each metal in the control algae.

The weighted average concentrations of trace elements in the control algae (excluding the very high values) were copper, 10.0, zinc 8.4, cadmium 0.21, lead 2.8, and thallium 0.3 ppm, fresh weight.

The levels of the selected metals in Dunkirk Harbor water were tested on March 1. They were Cu $<$ .01, Zn $<$ .02, Cd $<$ .001, Pb $<$ .005 ppm. This suggests that the algae growing in the harbor should be relatively free of these trace elements. However, *Ulothrix* is a sessile algae, and pieces of substrate including concrete and asphalt were collected with the algae. These mineral additions may have caused variations in the background levels of the metals in the algae as noted above.

Experimental Results and Discussion

The uptakes of the various metals by the algae in lab tests are shown in Tables C-3 to C-7. In each table, the amounts of metal added to the water and concentrations by AA analysis are shown. Concentrations of copper, zinc, cadmium, and lead were chosen to yield equal molar quantities for each metal. The molar quantities used were 0.02, 0.2, 2 and 5 moles x 10^{-6} per liter.

The theoretical and analyzed concentrations may differ depending upon the background level of the metal in the water, and upon the accuracy of the experimental procedures. The exposure time of the algae and the final concentration of the trace metal in the algae are given. The concentration rate is calculated as follows:

$$\underset{\text{(uptake/hr)}}{\text{Concentration rate}} = \frac{\text{conc. in exper. algae} - \text{conc. in control algae}}{\text{(time in hours) (conc. added to water)}}$$

Although a rate could be calculated, an equilibrium concentration was never reached nor does it seem to be achievable in live algae. Copper concentrations in the algae (Table C-3) were generally higher than the average control algae concentration of 10 ppm. The highest concentration, 764 ppm, occurred after exposure to 0.3 ppm soluble

TABLE C-3. Copper Uptake

1973 Date	ppm in Water		hours exposure time	ppm in algae	concentration rate ppm/hour	medium
	Amount Added	Amount Recovered				
2/6	0.127	0.110	48	256	40	tap water
2/8	0.317	0.270	24	764	99	" "
3/1	0.013	0.028	2.7	21	313	" "
3/1	0.013	0.028	17.5	12.5	11	" "
3/3	0.0013	<0.01	65	13.2	38	Algal Culture Medium
3/13	0.013	0.032	5	0.9	0	Spring Water

TABLE C-4 Zinc Uptake

1973 Date	ppm in Water		hours exposure time	ppm in Algae	Concentration rate ppm/hour	Medium
	Amount Added	Amount Recovered				
2/6	0.13	0.180	48	225	34	tap water
2/8	0.327	0.270	24	376	47	" "
3/1	0.013	0.035	2.7	11.2	80	" "
3/1	0.013	0.035	17.5	28.6	8.9	" "
3/3	0.0013	0.025	65	20.2	140	Algal Culture Medium
3/13	0.013	0.285	5	2.7	0	Spring Water

TABLE C-5. Cadmium Uptake

1973 Date	ppm in Water		Hours Exposure Time	ppm in Algae	Concentration rate ppm/hour	Medium
	Amount Added	Amount Recovered				
2/6	0.248	0.120	48	24	5	Tap Water
2/8	0.563	0.400	24	82	6	" "
3/1	0.023	0.028	2.7	2.1	30	" "
3/1	0.023	0.028	17.5	2.6	6	" "
3/3	0.0023	0.0035	65	9.4	61	Algal Culture Medium
3/13	0.023	0.015	5	0.2	0	Spring Water

TABLE C-6 Lead Uptake

1973 Date	ppm in Water		Hours Exposure Time	ppm in Algae	Concentration rate ppm/hour	Medium
	Amount Added	Amount Recovered				
2/6	0.412	0.270	48	86	10	Tap Water
2/8	1.03	0.520	24	906	36	" "
3/1	0.041	0.045	2.7	15.4	114	" "
3/1	0.041	0.045	17.5	1.0	0	" "
3/3	0.0041	0.0125	65	1.4	0	Algal Culture Medium
3/13	0.041	1.70	5	12.5	47	Spring Water

TABLE C-7 Thallium Uptake

1973 Date	ppm in Water		Hours Exposure Time	ppm in Algae	Concentration rate ppm/hour	Experiment
	Amount Added	Amount Recovered				
3/5	0.042	0.013	17	30.5	42	Loose Algae
3/7	0.211	0.250	1.1	29.9	127	Loose Algae
	0.211	0.250	19.5	354	86	Loose Algae
	0.005	0.004	1	1.4	220	Loose Algae
	0.005	0.004	19	2.3	21	Loose Algae
4/3	0.05		2.25	0.9	5	Loose Algae
4/4	0.05		23.5	8.2	7	Loose Algae
4/3	0.5		2.25	22.5	20	Loose Algae
4/4	0.5		23.5	44.0	4	Loose Algae
4/4	0.05	0.036	2.7	0.74	3	Tea Bag
	0.5	0.930	2.7	1.91	1	Tea Bag
	0.05		22.5	0.45	0	Tea Bag
	0.5		22.5	1.76	0	Tea Bag
	0.05	0.050	3	0.75	3	Tea Bag
	0.5	0.290	3	1.05	1	Tea Bag
	0.05		23	< 0.9	0	Tea Bag
	0.5		23	8.3	1	Tea Bag

copper for 24 hours. Exposure to quite small concentrations (plus 0.013 ppm) resulted in significant metal uptake in from 2.7 to 7.5 hours. The experiment with spring water was inconclusive. Concentration rates varied from 0 to 313 ppm/hour.

Zinc uptake (Table C-3) was quite high during exposure times of 24 to 48 hours for concentrations of 0.1-0.3 ppm soluble lead. At lesser additions of metal (plus 0.001 to plus 0.013) uptake was slightly above the average control algae concentration of 8.4 ppm. The experiment with spring water was inconclusive. Concentrations varied from 0 to 313 ppm/hour.

Cadmium uptake (Table C-4) was high during exposures to 0.1 to 0.56 ppm for times of 24 to 48 hours. The highest concentration, 82 ppm was found after 24 hours exposure to plus 0.56 ppm. The average level of 0.21 ppm calculated for control algae was exceeded in all experiments except that with spring water. Even at plus 0.0023 ppm, a concentration of 9.4 ppm was found in the algae after 65 hours. However, the concentration rates were quite low compared to the other metals varying from 0 to 61.

Lead uptake (Table C-5) was extremely high (906 ppm) after exposure to 1.0 ppm soluble lead for 24 hours. Exposure to 0.41 ppm resulted in a concentration in the algae of 86 ppm. Even at 0.04 ppm in the water, levels of 12.5 - 15.4 ppm occurred in the algae, exceeding the average control algal level of 2.8 ppm. Concentration rates vary from 1.0 to 906.

As discussed earlier, thallium uptake (Table C-6) was studied both with loose algae and with algae contained in tea bags. With loose algae, results are comparable to those obtained with copper, zinc, or lead. However, containment by "tea bags" limits the uptake of the metal. A short-time exposure of loose algae to 0.5 ppm of thallium resulted in an uptake of 22.5 ppm compared to an uptake of only 1.0 ppm by algae in tea bags. The effect of the tea bags on reducing the uptake rate of thallium is clearly shown by the concentration rates which varied from 0 to 3 with the bags, and from 4 to 220 without the bags.

Results of field testing were also not encouraging. Water flows through the clump of algae squeezed into a corner of the bag were insufficient. Multi-compartment bags are needed, anchored to the bottom of the stream and attached to a line at the surface so as to be kept normal to the water flow.

The enclosure of algae in the tea bags restricts uptake to an extreme degree. Thus, the method should not be useful for an analytical method unless a larger surface area of algae can be exposed.

The bioconcentration of trace metals observed in this study agrees with previous investigations. A new finding is the rapidity of which *Ulothrix* was able to concentrate some metals. Thus, with one hour exposure, the concentration factor for thallium was 127 to 220, and with 2.7 hours exposure, the factor for lead was 114, cadmium-30, zinc-80, and copper-313. The concentration factor refers to ppm of metal accumulated in algae per ppm excess in the water per hour. However, no clear cut pattern of metal uptake was observed among the various experiments.